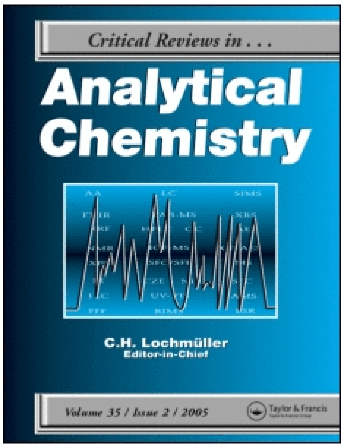
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Application of Stable Rradical-Containing Complexing Reagents for the Esr Determination of Metals

Vitalii Yu. Nagy; Oleg M. Petrukhin; Yurii A. Zolotov

To cite this Article Nagy, Vitalii Yu. , Petrukhin, Oleg M. and Zolotov, Yurii A.(1987) 'Application of Stable Rradical-Containing Complexing Reagents for the Esr Determination of Metals', Critical Reviews in Analytical Chemistry, 17: 3, 265 — 315

To link to this Article: DOI: 10.1080/10408348708542797

URL: http://dx.doi.org/10.1080/10408348708542797

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

APPLICATION OF STABLE RADICAL-CONTAINING COMPLEXING REAGENTS FOR THE ESR DETERMINATION OF METALS

Authors: Vitalii Yu. Nagy
Analytical Department
Institute of Microelectronics Technology
Problems and Superpure Materials
U.S.S.R. Academy of Sciences
Chernogolovka, Moscow District
Moscow, U.S.S.R.

Oleg M. Petrukhin
D. I. Mendeleev Institute of Chemical
Technology
Moscow, U.S.S.R.; and
Analytical Department
V. I. Vernadskii Institute of
Geochemistry and Analytical Chemistry
U.S.S.R. Academy of Sciences
Moscow, U.S.S.R.

Yurii A. Zolotov
Analytical Department
V. I. Vernadskii Institute of
Geochemistry and Analytical Chemistry
U.S.S.R. Academy of Sciences
Moscow, U.S.S.R.; and
Chemistry Department
Moscow State University
Moscow, U.S.S.R.

I. INTRODUCTION

The electron spin resonance (ESR) phenomenon, discovered by E. K. Zavoiskii in 1944 and widely employed in scientific research at present, can also be used as a method of chemical analysis for determining the concentrations of substances. The ESR method is based on the ability of atoms, ions, and molecules with unpaired electrons to absorb electromagnetic radiation of radio-frequency range in a constant external magnetic field.[1] The agreement of this process with the fundamental law of spectroscopy — the proportionality of the fraction of the radiation absorbed to the number of absorbing centers — enables the use of ESR in the determination of the concentration of paramagnetic particles using the appropriate reference samples.

Since 1960 various techniques were developed to determine several transition metals possessing paramagnetism in their basic oxidation states: copper(II),[2,251] chromium(III),[3,252] cobalt(II),[3] iron(III),[3-5,253] gadolinium(III),[6,254] manganese(II),[7,255] and vanadium(IV).[3,8,9,251] It also became possible to determine some metals nonparamagnetic under ordinary conditions by transforming them into less stable paramagnetic states: silver(II),[10,256] gold(II),[11] molybdenum(V),[12,13] titanium(III),[257] nickel(III),[14] rhenium(VI),[15] palladium(III),[16] platinum(III)[16] and rhodium(II).[258] ESR can also be applied for the determination of paramagnetic compounds: molecular oxygen, nitrogen oxides, chlorine dioxide, and free radicals.[17-20] Several reviews have been devoted to such analytical applications of ESR.[21-32,259-263,364]

ESR determination of paramagnetic substances, transition metals, in particular, exhibits a number of advantages, some of which that should be mentioned are the quickness of analysis, the possibility of continuous automatic control over the content of the components being determined in the flow, and applicability to samples in any aggregate state. Most ESR determinations are characterized by a very high selectivity, for example, gadolinium can be determined in the presence of any amounts of all the other rare-earth elements[6] or the determination of tungsten is possible in the presence of large amounts of molybdenum.[33] The use of ESR readily provides information about the content of a metal in the particular oxidation state, for instance, of vanadium(IV) alone.[3] Some metals have rather low detection limits. Thus, for molybdenum(V) in the form of $Mo(CNS)_5$ complex, this value makes up only 5×10^{-4} μg/mℓ or 5×10^{-9} g-ion/ℓ (a VARIAN E-4 ESR-spectrometer).[12] It should be mentioned, however, that the detection limit strongly depends on the line width in the ESR spectrum: the wider the line the higher the detection limit. Consequently, it depends on the nature of a paramagnetic ion and for a great number of metals the detection limits are much higher.

Therefore, ESR appears to have a certain analytical potential to be helpful for the solution of a number of special problems. In our opinion, the limited application of the method in analytical practice is due to the fact that highly sensitive ESR spectrometers are rarely available in laboratories that do inorganic analysis, the analytical basis of the method is not yet sufficiently developed, the number of metals under determination is restricted, and the detection limits with respect to the majority of paramagnetic ions are not very low.

New prospects of the application of ESR in chemical analysis became evident in recent years, owing to advances of organic chemistry in the synthesis of the compounds containing complexing groups in combination with fragments possessing unpaired electrons, i.e., free-radical complexing reagents. It now became possible to determine the concentrations of metal ions by binding them in complexes with these "spin-labeled" reagents and, subsequently, measuring the paramagnetism provided by peripheral (organic) parts of the coordination compound molecules formed.

Such an approach makes it possible to overcome the two restrictions inherent in ESR determinations of metal ions, based on the measurement of their intrinsic paramagnetism. On the one hand, the application of radical-containing reagents provides the determination of practically any metal, not only those possessing paramagnetic ions. On the other hand, the ESR spectra of organic free radicals, whose intensities are used to determine the concentrations of the metals bound to them, consist of much narrower lines than the spectra of most paramagnetic ions of transition metals. Hence, by using radical-containing reagents one can significantly lower the detection limits typical of direct ESR determinations of metals and make them less dependent on the nature of the element to be determined.

The present review considers the properties of stable radical-containing complexing compounds, which comprise the basis of their analytical application as well as the first procedures of ESR determination of metals with the aid of these unusual reagents. Since the properties of stable free radicals (with complexing groups, in particular) had been thoroughly studied from many viewpoints, it was impossible to cover all the literature published. Therefore, the aim of bibliographic fullness was taken with respect to two areas only: publications on analytical applications of free-radical reagents (the main subject of the review) and publications on syntheses and investigations of metal complexes of radical-containing (more exactly, nitroxide-containing) chelating reagents (the nearest of the adjacent subjects). The review covers the literature on these topics published up to 1985 inclusively. The references concerning other adjacent subject areas are given selectively; among these a reader can usually find the citations of fundamental publications able to provide complete and deep understanding of the phenomena in question.

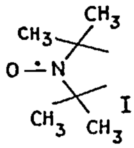
II. GENERAL CHARACTERISTICS OF RADICAL-CONTAINING COMPLEXING REAGENTS

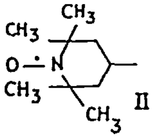
At present, the chemistry of stable free radicals is a broad independent field of chemical research. Numerous free radicals of various classes have been synthesized which retain their unpaired electrons, not only after a long period of storage, but also under various chemical and physical effects.[34-43]

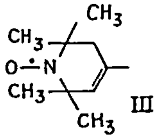
In principle, stable free radicals of several investigated classes can be used for ESR determination of metals. Thus, in specific cases, the uses of dithiolate radicals for the determination of nickel[264] and semiquinolate ones for the determination of copper,[265] zinc, cadmium, and lead[266] were reported.

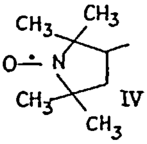
But of particular importance for analytical purposes are nitroxide radicals possessing an unpaired electron in the fragment $> N \overset{\cdot}{-} O$.[44,46] In contrast to stable free radicals of other classes whose stability is based mainly on the delocalization of an unpaired electron over the conjugated-bond system, nitroxide radicals combine stability with a very high degree of localization of the unpaired electrons on few atoms, mostly only on the oxygen-nitrogen bond. This peculiarity has made the synthesis of numerous derivatives of nitroxides possible without disturbing the unpaired electron, i.e., retaining the paramagnetism of the original radical. The reactions of this type have been described in a number of reviews and books.[42,45,47,48]

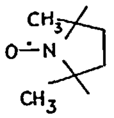
Among other substituents which have been introduced into nitroxide-containing molecules, there are various groups capable of bonding metal ions into complexes — into chelates, in particular. About 100 of such chelating compounds have been described. These reagents contain nitroxide groups in one of the following fragments:

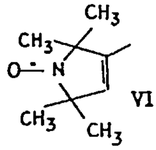

I

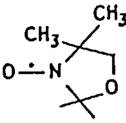

II

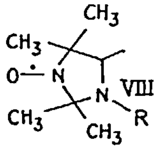

III

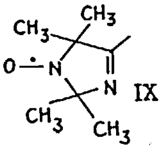

IV

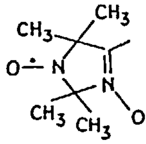

V

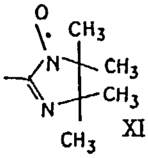

VI

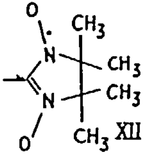

VII


VIII


IX


X


XI


XII

Among the reagents synthesized are the following (Table 1): β-diketones and other β-dicarbonyl compounds (1 to 14); various carboxylic acids (15 to 42); diol (43); monosubstituted phosphates (44 to 46); hydroxamic acid (47); crown-ether (48); reagents which combine a hydroxyl group with the heterocyclic nitrogen atom (49 and 50); amino acids (51 to 54, 57); oximes (58, 59, 80, 81); Schiff bases (60 to 75); oxyazo compound (76); reagents containing two imine nitrogen atoms or one imine nitrogen

Table 1
NITROXIDE-CONTAINING CHELATING REAGENTS

No.	Name (IUPAC nomenclature)	"Chemical Abstracts Service" Register No.	Ref.
1	4-(1,3-Dioxobutyl)-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	64818-89-9	49
2	4-(4,4,4-Trifluoro-1,3-dioxobutyl)-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	—	50
3	2,5-Dihydro-4-(3-methoxy-1,3-dioxopropyl)-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	64818-84-4	49
4	4-(3-Ethoxy-1,3-dioxopropyl)-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	64818-85-5	49
5	4-(1,3-Dioxobutyl)-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy 3-oxide	64818-88-8	49
6	2,5-Dihydro-4-(3-methoxy-1,3-dioxopropyl)-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy 3-oxide	64818-82-2	49
7	4-(3-Ethoxy-1,3-dioxopropyl)-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy 3-oxide	64818-83-3	49
8	2,2,6,6-Tetramethyl-4-(4,4,4-trifluoro-1,3-dioxobutyl)-1-piperidinyloxy	73704-87-7	51
9	3,6-Dihydro-2,2,6,6-tetramethyl-4-(4,4,4-trifluoro-1,3-dioxobutyl)-1(2H)-pyridinyloxy	69971-68-2	52
10	4-Hydroxy-2,2,6,6-tetramethyl-4-(4,4,4-trifluoromethyl-1,3-dioxobutyl)-1-piperidinyloxy	69971-64-8	52
11	4-([1,3-Dioxobutyl]oxy)-2,2,6,6-tetramethyl-1-piperidinyloxy	—	53
12	4-([4,4-Dimethyl-1,3-dioxopentyl]oxy)-2,2,6,6-tetramethyl-1-piperidinyloxy	73964-07-5	54
13	3-Formyl-2,2,6,6-tetramethyl-4-oxo-1-piperidinyloxy	71491-41-3	55
14	3-Formyl-2,2,5,5-tetramethyl-4-oxo-1-pyrrolidinyloxy	71491-42-4	55
15	4-Carboxy-2,2,6,6-tetramethyl-1-piperidinyloxy	37149-18-1	56
16	3-Carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	2154-68-9	57
17	3-Carboxy-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy	2154-67-8	57
18	4-(Carboxymethyl)-2,2,6,6-tetramethyl-1-piperidinyloxy	6599-87-7	58
19	4-(Carboxypropyl)-2,2,6,6-tetramethyl-1-piperidinyloxy	—	58
20	4-(Carboxypentyl)-2,2,6,6-tetramethyl-1-piperidinyloxy	—	58
21	3-(Carboxymethyl)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	—	58
22	3-(Carboxyethyl)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	—	58
23	3-(Carboxypropyl)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	—	58
24	3-(Carboxypentyl)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	—	58
25	4-(Carboxymethylene)-2,2,6,6-tetramethyl-1-piperidinyloxy	—	59
26	2-Carboxy-5,5,7,7-tetramethyl-1-oxa-6-azaspir o[2.5]o ct-6-yloxy	—	60
27	4-Carboxy-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy 3-oxide	49837-79-8	61
28	4-([3-Carboxy-1-oxo-2-propenyl]oxy)-2,2,6,6-tetramethyl-1-piperidinyloxy	—	62
29	4-([9-Carboxy-1-oxononyl]amino)-2,2,6,6-tetramethyl-1-piperidinyloxy	—	63
30	4-([3-Carboxy-1-oxo-2-propenyl]amino)-2,2,6,6-tetramethyl-1-piperidinyloxy	55557-76-1	64
31	4-([(3-Carboxy-1-oxo-2-propenyl)amino]methyl)-2,2,6,6-tetramethyl-1-piperidinyloxy	74799-77-2	64

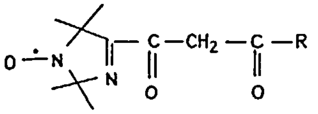
32	3-([3-Carboxy-1-oxo-2-propenyl]amino)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	26770-28-5	64
33	4-([2-Carboxybenzoyl]amino)-2,2,6,6-tetramethyl-1-piperidinyloxy	55967-42-5	64
34	4-([(2-Carboxybenzoyl)amino]methyl)-2,2,6,6-tetramethyl-1-piperidinyloxy	74813-22-2	64
35	3-([2-Carboxybenzoyl]amino)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	74799-78-3	64
36	4-(1,2-Dicarboxyethylidene)-2,2,6,6-tetramethyl-1-piperidinyloxy	3474-22-4	65
37	2-(15-Carboxypentadecyl)-2,5,5-trimethyl-1-pyrrolidinyloxy	69699-61-2	66
38	2-Butyl-2-(12-carboxydodecyl)-5,5-dimethyl-1-pyrrolidinyloxy	66978-86-7	47
39	2-(7-Carboxyheptyl)-2,5-dimethyl-5-nonyl-1-pyrrolidinyloxy	66610-23-9	67
40	2-(2-Carboxyethyl)-4,4-dimethyl-2-tetradecyl-3-oxazolidinyloxy	35545-52-9	63
41	2-(14-Carboxytetradecyl)-2-ethyl-4,4-dimethyl-3-oxazolidinyloxy	53034-38-1	68
42	(2-Carboxy-1,1-dimethylethyl)(2-hydroxy-1,1-dimethylethyl)nitroxide	—	69
43	4-Hydroxy-3-(hydroxyphenylmethyl)-2,2,6,6-tetramethyl-1-piperidinyloxy	69247-78-5	70
44	2,2,6,6-Tetramethyl-4-(phosphonooxy)-1-piperidinyloxy	22690-04-6	71
45	4,5-Dihydro-4,4,5,5-tetramethyl-2-(3-[phosphonooxy]-2-[2-pyridinyl]propyl)-1H-imidazol-1-yloxy 3-oxide	40525-55-1	72
46	4-([Hydroxy([hydroxy(phosphonooxy)phosphinyl]oxy)phosphinyl]oxy)-2,2,6,6-tetramethyl-1-piperidinyloxy	37070-46-5	73
47	3-Hydroxy-2,2,5,5-tetramethyl-4-oxo-1-imidazolidinyloxy	69826-44-4	74
48	2,2,6,6-Tetramethyl-4-([(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-yl)carbonyl]oxy)-1-piperidinyloxy	66480-90-8	75
49	2,5-Dihydro-4-(1-hydroxyethyl)-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	66250-75-7	76
50	2,2,5,5-Tetramethyl-4-(2-oxo-2-phenylethylidene)-1-imidazolidinyloxy	84271-26-1	77
51	4-Amino-4-carboxy-2,2,6,6-tetramethyl-1-piperidinyloxy	15871-57-5	78
52	3-Amino-4-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	15871-58-6	78
53	*N*-([(2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)oxy]carbonyl)-L-phenylalanine	71645-10-8	79
54	*N*-([(2,2,6,6-Tetramethyl-1-oxy-4-piperidinyl)oxy]carbonyl)-L-tryptophan	71645-13-1	79
55	4-Carboxy-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	36097-86-6	80
56	2-(2-Carboxy-2-[2-pyridinyl]ethyl)-4,5-dihydro-4,4,5,5-tetramethyl-1H-imidazol-1-yloxy 3-oxide	40525-75-5	81
57	3-(Bis[carboxymethyl]amino)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	74291-01-3	82
58	2,5-Dihydro-4-([hydroxyimino]methyl)-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy 3-oxide	49837-81-2	61
59	2,5-Dihydro-4-(1-[hydroxyimino]ethyl)-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy 3-oxide	60829-52-9	83
60	2,2,6,6-Tetramethyl-4-(salicylideneamino)-1-piperidinyloxy	23504-55-4	84
61	4-([(2-Hydroxy-3-methoxyphenyl)methylene]amino)-2,2,6,6-tetramethyl-1-piperidinyloxy	74093-24-6	85
62	4-([(3-Formyl-2-hydroxy-5-methylphenyl)methylene]amino)-2,2,6,6-tetramethyl-1-piperidinyloxy	62885-55-6	86
63	4-([(2-Hydroxy-naphthalenyl)methylene]amino)-2,2,6,6-tetramethyl-1-piperidinyloxy	35846-16-3	87
64	4-([([2-Hydroxy-1-naphthalenyl]methylene)amino]methyl)-2,2,6,6-tetramethyl-1-piperidinyloxy	—	86
65	4-([([3-Formyl-2-hydroxy-5-methylphenyl]methylene)amino]methyl)-2,2,6,6-tetramethyl-1-piperidinyloxy	62939-18-8	86
66	2,2,5,5-Tetramethyl-3-(salicylideneamino)-1-pyrrolidinyloxy	23504-56-5	84
67	3-([(5-Chloro-2-hydroxyphenyl)methylene]amino)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	72093-38-0	88
68	3-([(5-Bromo-2-hydroxyphenyl)methylene]amino)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	68792-00-7	88

Table 1 (continued)
NITROXIDE-CONTAINING CHELATING REAGENTS

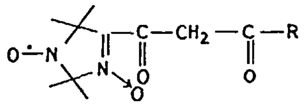
No.	Name (IUPAC nomenclature)	"Chemical Abstracts Service" Register No.	Ref.
69	3-([(2-Hydroxy-5-nitrophenyl)methylene]amino)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	72093-39-1	88
70	3-([(2-Hydroxy-3-methoxyphenyl)methylene]amino)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	74093-25-7	85
71	3-([(3-Formyl-2-hydroxy-5-methylphenyl)methylene]amino)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	51842-52-5	86
72	3-([(2-Hydroxy-1-naphthalenyl)methylene]amino)-2,2,5,5-tetramethyl-1-pyrrolidinyloxy	39705-89-0	87
73	4,4′-([2-Hydroxy-5-methyl-1,3-phenylene]bis[methylidynenitrilo])bis(2,2,6,6-tetramethyl-1-piperidinyloxy)	62885-56-7	86
74	4,4′-([2-Hydroxy-5-methyl-1,3-phenylene]bis[methylidynenitrilomethylene])bis(2,2,6,6-tetramethyl-1-piperidinyloxy)	—	86
75	3,3′-([2-Hydroxy-5-methyl-1,3-phenylene]bis[methylidynenitrilo])bis(2,2,5,5-tetramethyl-1-pyrrolidinyloxy)	62939-17-7	86
76	4-([2-Hydroxyphenyl]azomethylene)-2,2,3,5,5-pentamethyl-1-imidazolidinyloxy	—	89
77	4,5-Dihydro-4,4,5,5-tetramethyl-2-(2-pyridinyl)-1H-imidazol-1-yloxy 3-oxide	38987-15-4	90
78	2-(6-Bromo-2-pyridinyl)-4,5-dihydro-4,4,5,5-tetramethyl-1H-imidazol-1-yloxy 3-oxide	56664-63-2	90
79	4,4,4′,4′,5,5,5′,5′-Octamethyl-(2,2′-bi-2-imidazoline)-1,1-diyldioxy 3-oxide	25105-78-6	91
80	2,5-Dihydro-4-([hydroxyimino]methyl)-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	52213-23-7	61
81	2,5-Dihydro-4-(1-[hydroxyimino]ethyl)-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	60829-53-0	92
82	4,5-Dihydro-4,4,5,5-tetramethyl-2-(2-pyridinyl)-1H-imidazol-1-yloxy	50599-35-4	93
83	2-(6-Bromo-2-pyridinyl)-4,5-dihydro-4,4,5,5-tetramethyl-1H-imidazol-1-yloxy	56664-61-0	90
84	4,4,4′,4′,5,5,5′,5′-Octamethyl-(2,2′-bi-2-imidazoline)-1,1′-diyldioxy	25105-79-7	91
85	4,4′-(1,2-Ethanediylidenedinitrilo)bis(2,2,6,6-tetramethyl-1-piperidinyloxy)	42592-37-0	94
86	4,4′-(1,2-Ethanediylidenebis[nitrilomethylene])bis(2,2,6,6-tetramethyl-1-piperidinyloxy)	59049-86-4	95
87	3,3′-(1,2-Ethanediylidenedinitrilo)bis(2,2,5,5-tetramethyl-1-pyrrolidinyloxy)	59049-85-3	95
88	4-([Aminothioxomethyl]hydrazono)-2,2,6,6-tetramethyl-1-piperidinyloxy	35330-54-2	96
89	4-([(Aminothioxomethyl)hydrazono]methyl)-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	70345-97-0	97
90	4-(1-[(Aminothioxomethyl)hydrazono]ethyl)-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	70345-98-1	97
91	4-([(Aminothioxomethyl)hydrazono]methyl)-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy 3-oxide	70345-99-2	97
92	4-([Dithiocarboxy]oxy)-2,2,6,6-tetramethyl-1-piperidinyloxy potassium salt	25884-46-2	98
93	4-(1-[(Dithiocarboxy)oxy]ethyl)-2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy	—	99
94	2,5-Dihydro-2,2,5,5-tetramethyl-4-phenyl-1H-imidazol-1-yloxy	39753-69-0	100
95	2,5-Dihydro-2,2,5,5-tetramethyl-4-phenyl-1H-imidazol-1-yloxy 3-oxide	18796-03-7	205

atom with N-oxide group (77 to 87); thiosemicarbazones (88 to 91); and xanthates (92, 93). Also described is compound 94 which is capable of chelating metals by means of coordinating them towards the imine nitrogen atom and forming the bond between the metal and orthocarbon atom of phenyl.

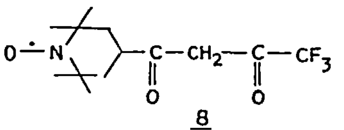
O,O-Type Reagents



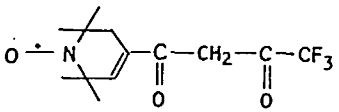
1, R=CH_3; 2, R=CF_3;
3, R=OCH_3; 4, R=OC_2H_5;



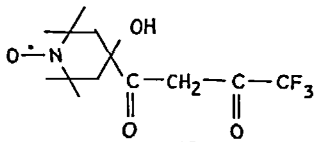
5, R=CH_3; 6, R=OCH_3;
7, R=OC_2H_5;



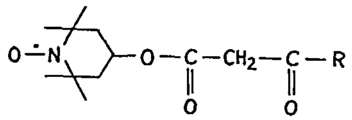
8



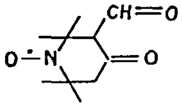
9



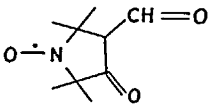
10



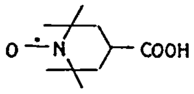
11, R=CH_3; 12, R=t-Bu



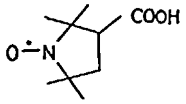
13



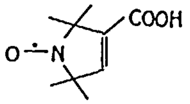
14



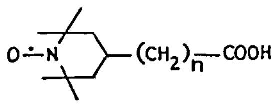
15



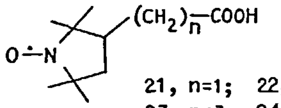
16



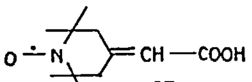
17



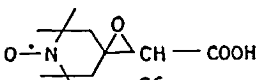
18, n=1; 19, n=3; 20, n=5



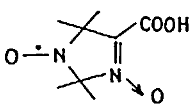
21, n=1; 22, n=2;
23, n=3; 24, n=5



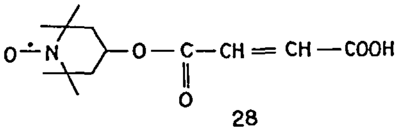
25



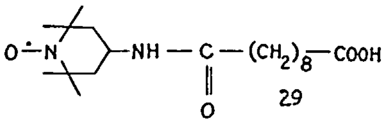
26



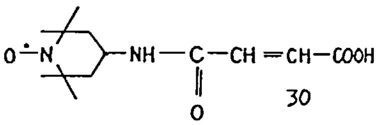
27



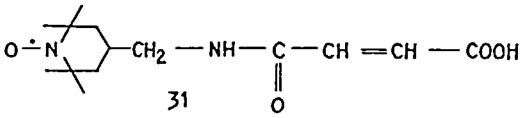
28



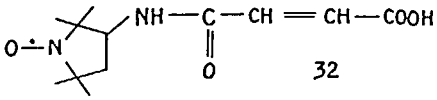
29



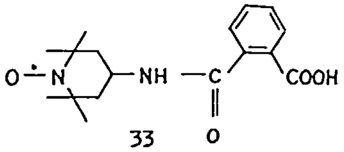
30



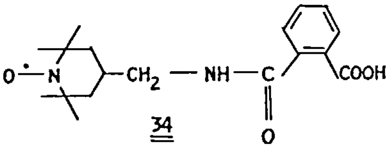
31



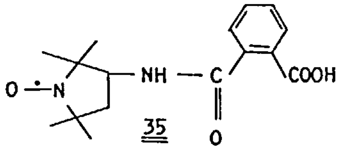
32



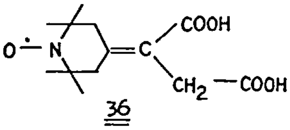
33



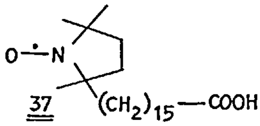
34



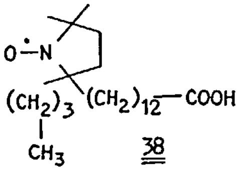
35



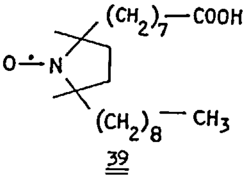
36



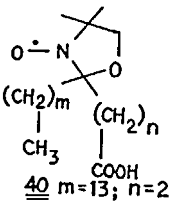
37



38

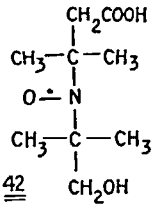


39

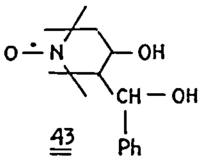


40 m = 13; n = 2

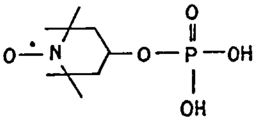
41 m = 1; n = 14



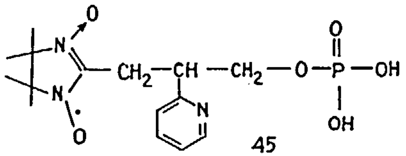
42



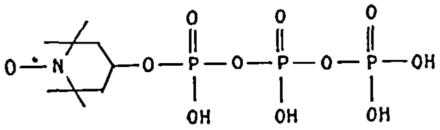
43

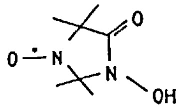


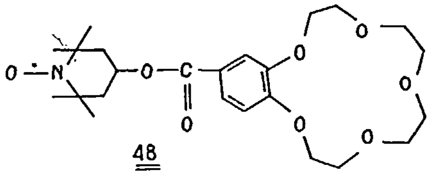
44



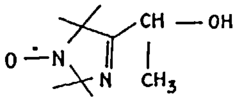
45

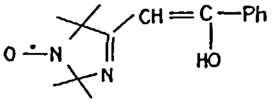

46

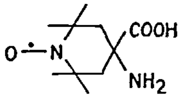

47

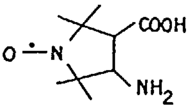

48

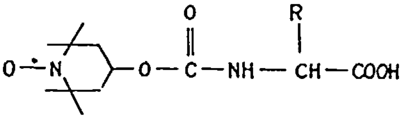
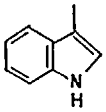
N,O-Type Reagents

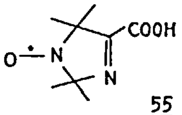

49

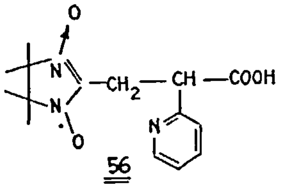

50

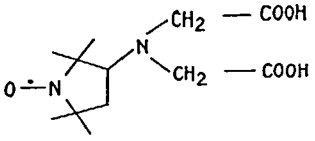

51

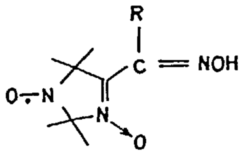

52

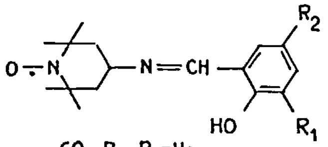

53, $R = -CH_2-Ph$; 54, R= 

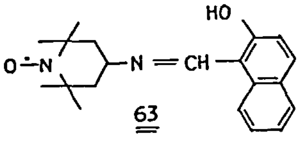

55

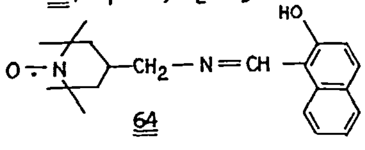

56

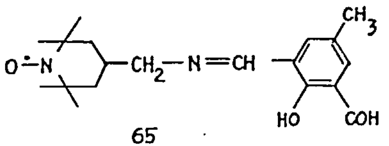

57


58, R=H; 59, $R=CH_3$

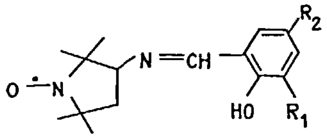

60, $R_1=R_2=H$;
61, $R_1=OCH_3$; $R_2=H$;
62, $R_1=COH$; $R_2=CH_3$;


63

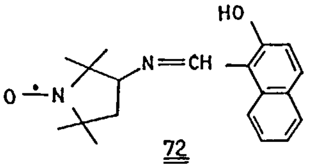

64



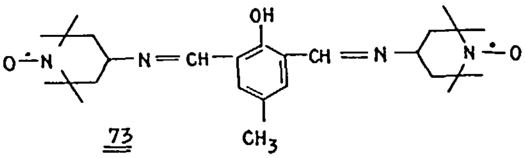
65



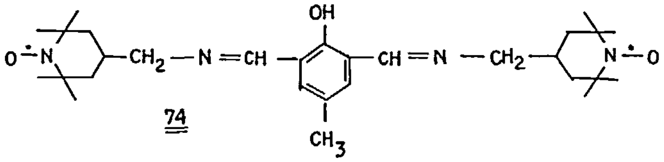
66, $R_1=R_2=H$;
67, $R_1=H$; $R_2=Cl$;
68, $R_1=H$; $R_2=Br$;
69, $R_1=H$; $R_2=NO_2$;
70, $R_1=OCH_3$; $R_2=H$;
71, $R_1=COH$; $R_2=CH_3$



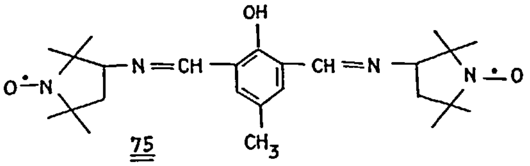
72



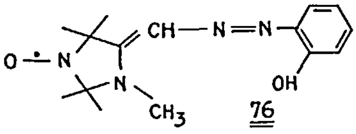
73



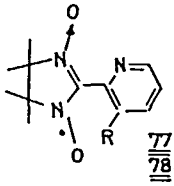
74



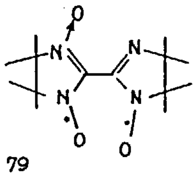
75



76

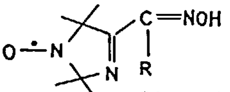


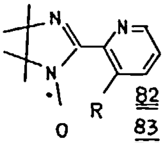
77, R=H;
78, R=Br

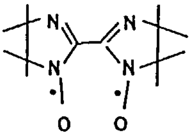


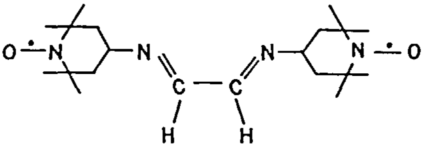
79

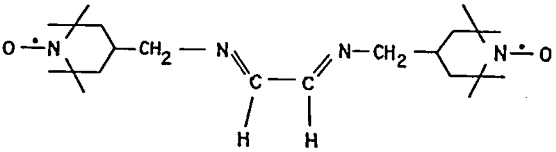
N,N-Type Reagents

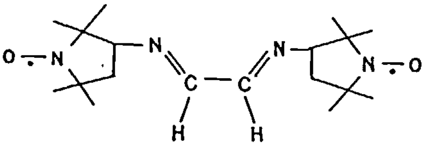

80, R=H;
81, R=CH$_3$;


82, R=H;
83, R=Br

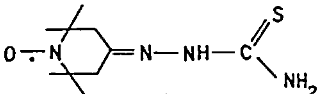

84

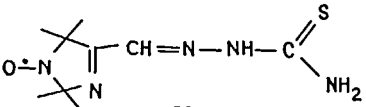

85

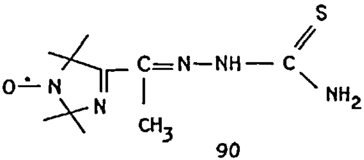

86

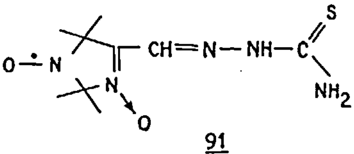

87

N,S-Type Reagents

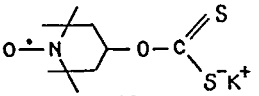

88

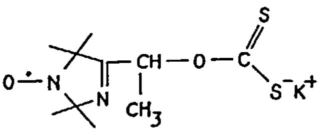

89


90

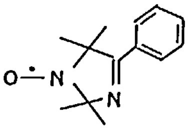

91

S,S-Type reagents

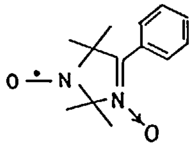

92


93

Reagents, forming chelates with carbon - metal bond



94



95

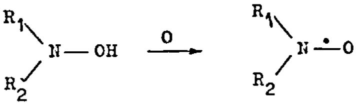
Besides the structures shown, the following nitroxide chelating reagents were described: enaminoketones,[267] semicarbazones,[268,269] α-carbonyl- and hydroxymonooximes,[270] other crown-ethers,[271,281] oxaminic acid,[272] new Schiff bases,[273] iminoamino- and diaminocompounds,[74,274] pyridyl- and imidazolylazomethines,[274-277] porphyrins,[215,278,314] amidoximes,[279,280] alizarin derivatives,[282,283] dithiocarbamate,[284] enaminothiones,[285] reagents with the oxime group nearby nitroxide,[286,287] compounds containing nitroxide radical, and a fluorescent fragment connected by aminocarbonyl and thiourea chelating groups.[267,288]

Therefore, the range of the reagents synthesized which contain the spin label in the form of nitroxide radical is rather wide and various. They are represented by well-known classes of organic analytical reagents, their diamagnetic analogs being widely used in inorganic analysis. Further on we consider a number of problems concerning this new group of complexing reagents.

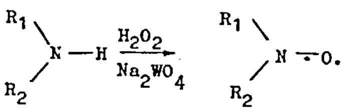
A. Synthesis

The synthesis of nitroxide-containing complexing reagents conventionally consists of obtaining the radical label (the fragment N—O) and "designing" the complexing group.

The first problem can be solved by means of two most widely used techniques, namely, dehydrogenation of the corresponding hydroxylamine (for example, with the aid of lead dioxide):[104-106]



and oxidation of secondary amine (oxidizing agents are per acids, hydrogen peroxide in the presence of tungstates, and others):[107-109]



In most cases, these reactions proceed quite readily and do not represent any procedural difficulties.

The second part is a conventional organic synthesis which is distinguished only by the necessity to retain the radical centers. In many cases, this difficulty can be successfully overcome by using specific techniques, though sometimes it becomes a serious obstacle in creating new types of reagents. Thus, a comparatively small number of sulfur-containing compounds among spin-labeled complexing reagents is accounted for by the difficulty of preserving the nitroxide radical in the presence of sulfur (especially —SH groups) in the reaction system.

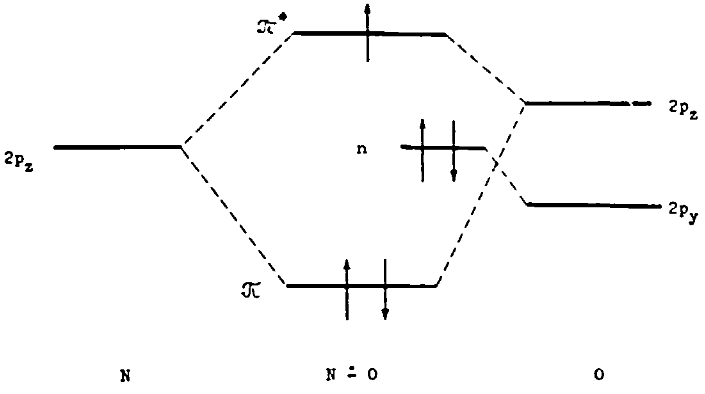


FIGURE 1. Molecular orbitals of isolated nitroxide group.

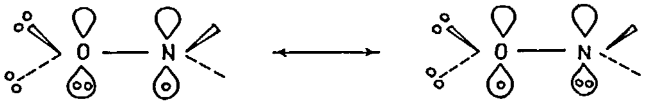
The methods of obtaining the nitroxide-containing compounds with various substituents were considered in general form in a number of books and reviews;[35,36,38-40,42-45,47,101-103] the procedures of the synthesis of specific chelating reagents are described in the works referred to in Table 1. Today it has become apparent that obtaining the nitroxide-containing reagents is a task only a little more complicated than the synthesis of diamagnetic organic compounds. A large range of nitroxide-containing compounds (mostly used for research in molecular biology) is being manufactured by a number of firms.

B. Electron Structure

The nitroxide group > N−O is a specific structural fragment of the reagents considered herein, which produces the ESR signal and allows the determination of the concentrations of metals bound to them. The electron structure of this unusually stable radical element was the subject of numerous theoretical and experimental investigations (see, for example, Berthier et al.[110-120]).

The results of quantum-mechanical calculations, which are in good agreement with the data of experimental methods including ESR (see below), have shown that in the compounds which do not contain multiple bonds in the α position with respect to nitroxide (fragments I-X), the unpaired electron is practically completely concentrated on the nitrogen-oxygen bond. In such molecules, the nitroxide group could be considered with good approximation irrespective of the other parts of the structure, and its electron state could be described through a set of molecular orbitals represented in Figure 1.[42] The unpaired electron is placed on the antibonding π orbital formed by $2p_z$-orbitals of the nitrogen and oxygen atoms. The part of the s-state in the wave function of the unpaired electron for the nitroxide-containing compounds of the types under consideration does not exceed 3%,[38,42] therefore, these compounds can be considered as typical π-electron radicals. The hydridization of the nitrogen atom orbitals is close to sp^2.

In the molecules of the reagents with fragments I-X, the unpaired electron is delocalized only between the two atoms — nitrogen and oxygen:



The distribution of the spin density between these atoms depends on the structure of other parts of the molecule in a very slight degree; the ratio $\varrho_O^\pi/\varrho_N^\pi$ is approximately equal to 7:3.[110-115,120]

The estimates based on the experimental value of the dissociation energy of N—O bond in the > N—OH group[121] and on the thermodynamic characteristics of 4-oxo- and 4-hydroxyderivatives of piperidine show that the energy of delocalization of an unpaired electron on a nitrogen-oxygen bond of the nitroxide group makes up a rather high value approximately equal to 130 kJ/mol.[44] This is one of the major reasons for the stability of nitroxide radicals.

In the molecules of most reagents with fragments XI and XII, the unpaired electron is delocalized along the chain O—N—C—N(—O). The distribution of the spin density in such systems is markedly influenced by the nature of the substituent at the carbon atom in position 2, the cycle conformation, and protonation of the nitrogen atom or the N → O group.[122]

C. Spatial Structure

The data on spatial structure of the molecules of a nitroxide-containing reagent are helpful for developing analytical methods, since they make it possible to predict or exclude the possibility of simultaneous coordination of the metal ion both by the chelating group (or its part) and the $N\dot{-}O$ group. Such a process results in a sharp change in the ESR radical spectrum, which can markedly affect the characteristics of the analytical method.

The quantum-mechanical calculations performed for the $H_2NO\cdot$ molecule have shown that the energies of interconformation transitions in this system are negligible and the radical does not possess a distinct geometry.[123,124] The results of numerous X-ray diffraction investigations of nitroxide-containing compounds summarized in reviews[125,126,289,290] have confirmed that the geometry of the fragment > $N\dot{-}O$ is completely determined by the geometry of other parts of the molecule. This fragment is either flat or has the form of a pyramid. The angle formed by the plane of the CNC bonds and the $N\dot{-}O$ bond can reach 22° in the latter case. Five-membered nitroxide-containing cycles are usually flat, while six-membered ones have either the "chair" conformation or the twist conformation. The length of the $N\dot{-}O$ bond in the majority of the compounds investigated equals 1.25 to 1.30 Å, that is, less than the length of the single N—O bond (1.34 Å), though noticeably exceeds the length of the double N=O bond (0.99 Å).

The structure of some nitroxide-containing chelating reagents in the crystalline state is completely deciphered, with all the interatom distances and angles between the bonds being determined.[126,289]

On the basis of the data obtained, one can assume that for the great majority of synthesized reagents, the simultaneous coordination of the metal by nitroxide and chelating groups is impossible spatially. For some reagents (for instance, 40, 42, 82, and 83) such coordination can be theoretically possible and seems probable,[93,299] but there are no inambiguous experimental results yet which would reliably confirm its implementation.

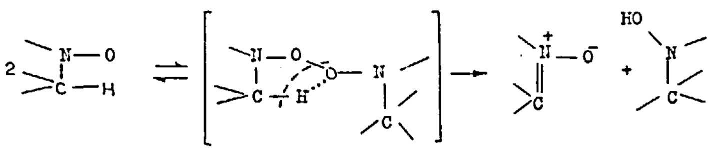
D. Stability

The nitroxide radicals are much more stable than the stable radicals of other classes. Many nitroxide-containing compounds do not noticeably lose their paramagnetism after many years of storage. These compounds retain their free valencies in the media of organic solvents as well as in not very acidic aqueous solutions. Among the reasons for this stability, unusual for free radicals, are the inherent stability of the three-electron configuration of the nitrogen-oxygen fragment, steric factors preventing dimerization and disproportionation, and additional delocalization of the unpaired electron occurring in some nitroxide-containing heterocycles (XI, XII).[41,42,121,127,128]

However, stability of nitroxide radicals is not unlimited: under certain conditions the nitroxide-containing compounds can take part in chemical reactions which are followed by the loss of paramagnetism. In developing analytical methods, it is of importance to take into account the possibility of such processes, since it is very significant for the accuracy of determinations to retain quantitatively the nitroxide groups. The reactions resulting in the decay of nitroxide groups comprise disproportionation, interaction with other free radicals, reactions with strong acids, monoelectron reduction, and monoelectron oxidation.

1. Disproportionation

Disproportionation is a common property of free radicals. However, a specific feature of the mechanism of this process within the class of nitroxides consists of the participation of the hydrogen atom which is in the α position with respect to the N$\dot{-}$O group.[129,130]



The reaction results in the formation of diamagnetic derivatives of hydroxylamine and nitrone which can undergo further transformations.[131] Hindrances due to the disproportionation reaction can be easily avoided if the range of spin-labeled analytical reagents used is confined by compounds with the quaternary carbon atoms in the positions nearest to the nitroxide. The structures of all the chelating reagents mentioned above meet this requirement.

2. Interaction with Free Radicals

Nitroxide radicals are capable of recombining with active radicals of other classes to form diamagnetic hydroxylamine ethers:[35,132,133]

Since free radicals are not found to be formed in analytical systems frequently, there should be no serious limitations in the application of nitroxide-containing compounds in analytical chemistry.

3. Interaction with Strong Acids

Destruction of nitroxide radicals in concentrated solutions of strong acids essentially is the reaction of disproportionation resulting in the formation of diamagnetic salts of hydroxylamine and oxaammonium:[127,134,158]

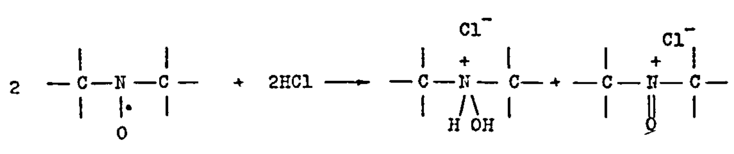
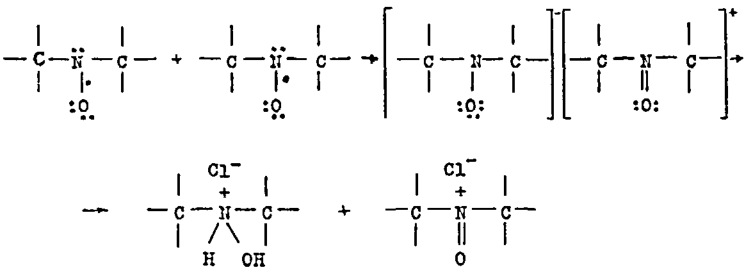


Table 2
STABILITY OF PARAMAGNETIC CENTERS OF 2,2,6,6-TETRAMETHYL-4-OXO-PIPERIDINYLOXY IN AQUEOUS SOLUTIONS OF ACIDS[138] (RADICAL CONCENTRATION 0.01 *M*)

Time of staying in acid (min)	Share of radicals retained (%)											
	Sulfuric acid				Perchloric acid				Hydrochloric acid			
	0.1 *N*	0.5 *N*	1 *N*	2 *N*	0.1 *N*	0.5 *N*	1 *N*	2 *N*	0.1 *N*	0.5 *N*	1 *N*	2 *N*
20	99	92	80	60	97	89	72	36	97	86	68	9
60	96	78	58	32	94	74	49	7	92	68	42	0
120	94	66	37	10	90	58	28	1	87	52	21	0

It was assumed that the acid is responsible only for the equilibrium shift towards the formation of diamagnetic products due to protonation of the hydroxylamine anion formed:[135]



But other results have shown that the protonation stage appears to precede disproportionation, the nitroxide protonated retaining its paramagnetism.[136,158]

The oxaammonium salt obtained upon disproportionation can undergo further transformations,[135] and generally the process is irreversible. There exists opinion that the degree of the stability of nitroxide in acidic solutions is basically determined by the speed of these irreversible reactions.[137]

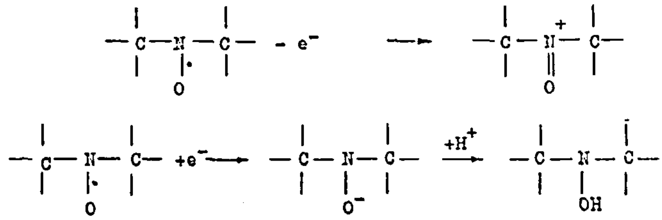
In analytical practice it is of great importance to know the limits of the pH range in which the speed of nitroxide radicals decay is negligible. The data for radical 96 are given in Table 2. The data concerning the stability of other compounds are limited; some fragmental literature data and our own experience make possible the conclusion that in acid solutions with pH above 2 to 3, the stability of most nitroxide radicals is quite sufficient for the implementation of analytical operations of usual duration.

96

Nitroxide radicals — derivatives of imidazoline (containing an unpaired electron in the fragments IX to XII) — are more resistant to the action of acids than the piperidine derivatives (fragment II).[42,48,139,140] This phenomenon is accounted for by greater affinity to proton of the nitrogen atom in position 3 or the nitron group (as compared to nitroxide) which is contained in the imidazoline cycle. The positive charge nearby the nitroxide group, resulting from the primary protonation of these additional fragments, prevents the approaching of the second proton to the nitroxide. On the other hand, the protonation of the nitrogen atom in position 3 leads to inductive withdrawal of the nitroxide oxygen atom electron pair, thus decreasing the basicity of nitroxide moiety. The two factors impede the process of nitroxide group protonation and thus increase the stability of the spin label.[48]

4. Oxidation and Reduction

The reactions of nitroxide radicals with external oxidizing and reducing agents can be schematically represented by the following equations:



The values of standard electron potentials for such systems are not given in literature, therefore, the oxidation-reduction ability of nitroxides can be estimated only through the results of voltamperometric investigations.[127,141-147] The potentials of monoelectron oxidation of most nitroxide radicals at the platinum electrode in acetonitrile are found to be in the range of 0.2 to 0.6 V (saturated calomel electrode), and the reduction potential of compound 96 in the aqueous medium at the mercury electrode depends on pH and in neutral solution is equal to (with respect to saturated calomel electrode) −0.13 V.[141] These data lead to the conclusion that nitroxide radicals can be affected only by strong oxidizing agents, but also by both strong and moderate reducing agents.

The oxidation reactions of nitroxides with molecular chlorine and bromine,[134,149] antimony(V) and tin(IV) halides,[150,151] triphenylmethylcarbonium salts,[152] and oxygen in the presence of silver oxide[135] are described.

In most cases, to reduce a nitroxide both electron donor and a proton donor are required. The reduction reactions of nitroxide radicals in acidic media with the aid of elementary alkali metals, zinc and tin,[42] as well as hydrogen peroxide,[153] iodide ions,[60] gaseous hydrogen chloride and bromide,[147] hydrogen sulfide,[42] hydrogen in the presence of platinum,[148] and iron(II),[154] are known.

Of practical importance are the reduction reactions of nitroxides with phenylhydrazine[155] and ascorbic acid.[156] Since these reactions proceed stoichiometrically, quantitatively, and fast (within minutes), they make possible selective transformation of a radical into a corresponding diamagnetic hydroxylamine, the fact is of importance, particularly for NMR investigation of nitroxide-containing molecules.

Recent investigations have shown that the resistance of cyclic nitroxide radicals to reduction increases with a decrease of the cycle size.[157]

Analysis of the data concerning the reactions which result in the destruction of nitroxide radicals leads to a conclusion that though such processes require attention of the analyst in developing the procedures for the determination of metals, they not too seriously confine the application area of nitroxide-containing chelating reagents. Most reactions of chelate formation proceed in not very acidic solutions. The oxidizing and reducing reagents listed above are rather rarely met in analytical systems: if present, they should be separated or neutralized prior to spin-labeled reagent addition, or the determination should be performed in conditions preventing red-ox process (in alternative pH range, for instance).

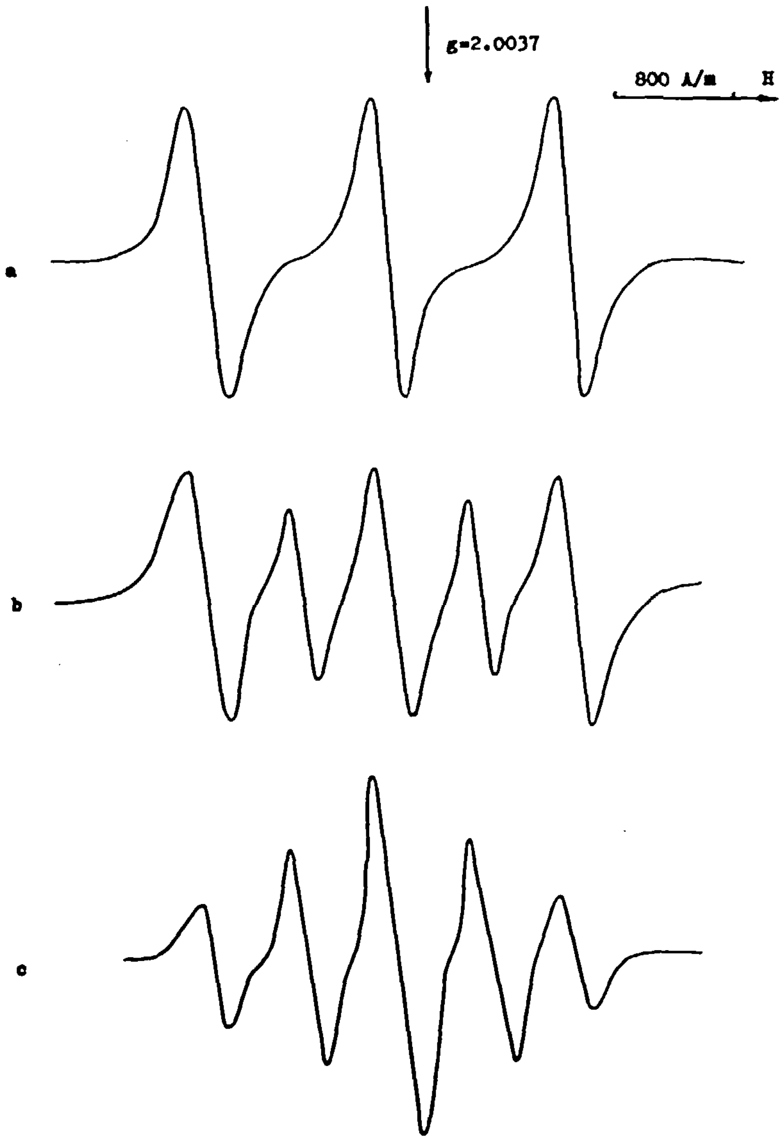


FIGURE 2. Typical ESR spectra of nitroxide-containing reagents in nonviscous solutions. (a) Monoradical reagents with I-X fragments; (b) biradical reagents with I-X fragments; (c) monoradical reagents with XI or XII fragments.

In the conditions of the majority of analytical systems the nitroxide radicals are retained quantitatively, which permits one to handle them in just the same way as traditional organic analytical reagents. Sometimes, even more important than the decay of radicals is the destruction of the chelating group of the spin-labeled compounds. Such a destruction is certainly typical of some usual, diamagnetic reagents, though in this case the process is not always noticeable and often can be neglected.

E. ESR-Spectroscopic Properties

Chelating reagents containing an unpaired electron in the fragments I-X produce in nonviscous solutions a ESR spectrum comprising three equidistant lines of equal intensity (Figure 2a).[38,42,291-294] The spectrum of such a type is due to the interaction of spins of the unpaired electron and the nitrogen ^{14}N atom nucleus (natural content 99.63%, I = 1). The hyperfine structure resulting from the interaction of the unpaired electron with the protons of the four closely situated methyl groups does not resolve under usual conditions, but it can usually be observed, if molecular oxygen broadening spectral lines are removed out of the solution. The splittings from neighboring magnetic nuclei are not very important for quantitative metal determinations at present, but they are crucial to qualitative analysis of unstable free radicals by the spin-trapping method.[295] A comparatively simple structure of nitroxide ESR spectra is indicative of the localization of the unpaired electron in these fragments at the $N\dot{-}O$ group.

The g-factor slightly depends on the nature of the chelating group and is close to 2.006. The hyperfine interaction constant with ^{14}N almost does not depend on the chelating group either and is approximately equal to 1200 A/m (15 Oe). The halfwidths of the lines are equal to 80 to 160 A/m (1 to 2 Oe), i.e., it is much less than the halfwidths of the lines in the ESR spectra of most paramagnetic metal ions spreading from dozens to thousands of Oersted.

The reagents containing two fragments of II-X types (so-called biradicals) produce a similar triplet ESR spectrum only when there is no spin-spin interaction between the two paramagnetic centers in the molecule. In the case of spin-spin interaction (which can proceed over the bond system of the molecule, by direct overlapping the molecular orbitals of the unpaired electrons or through the solvent molecules[42,101]) the spectrum can comprise five or more lines (Figure 2b). The investigations of spin-spin interactions in biradicals and their influence upon the ESR spectra are reviewed in numerous works.[101,159,160]

The ESR spectra of solutions of reagents possessing radical-containing fragments XI and XII exhibit a quintet of lines with the intensity ratio 1:2:3:2:1 (Figure 2c). Such a spectrum is due to the interaction of the unpaired electron spin with the spins of two ^{14}N nuclei.[1]

The ESR spectra of nitroxide-containing compounds are sensitive to the nature of the solvent, temperature, and the presence of foreign paramagnetic particles in solution.[161-169,296-298] This sensitivity can be explained by the dependence upon the above-mentioned factors of such determining ESR spectrum processes as rotation and motion of the radical-containing molecules, their solvation, exchange, and dipole interaction with each other and with foreign paramagnetic ions and molecules.

Proportion between the ESR spectrum intensity of nitroxide radicals and their concentration makes possible the application of ESR for the determination of nitroxide-containing compounds. The measure of the concentration of a paramagnetic substance is the area under the curve of the entire absorption spectrum or its one line. Since the modern ESR spectrometers record the first derivative of the spectrum curve rather than the ordinary "integral" spectrum curve, double integration is required to calculate the unknown area (Figure 3a). This problem can be comparatively easily solved with the aid of microcomputers; in many cases, however, the intensities can be characterized using even more easily available values.

Thus, if the shape of the spectrum line does not depend on the concentration of the substance being determined, the measure of the area under the integral absorption curve can be represented by the product of the amplitude of the first derivative curve by the square distance between the points of the integral curve maximum slope (Figure 3b). However, if by changing the concentration not only the shape of the spectrum line remains constant, but also its halfwidth, the amplitude of the first derivative curve can be used as a measure of concentration (Figure 3c).

In most cases of metal determinations with nitroxide radicals it is possible to use this simple measure. However, when the method is being developed, it is necessary to make

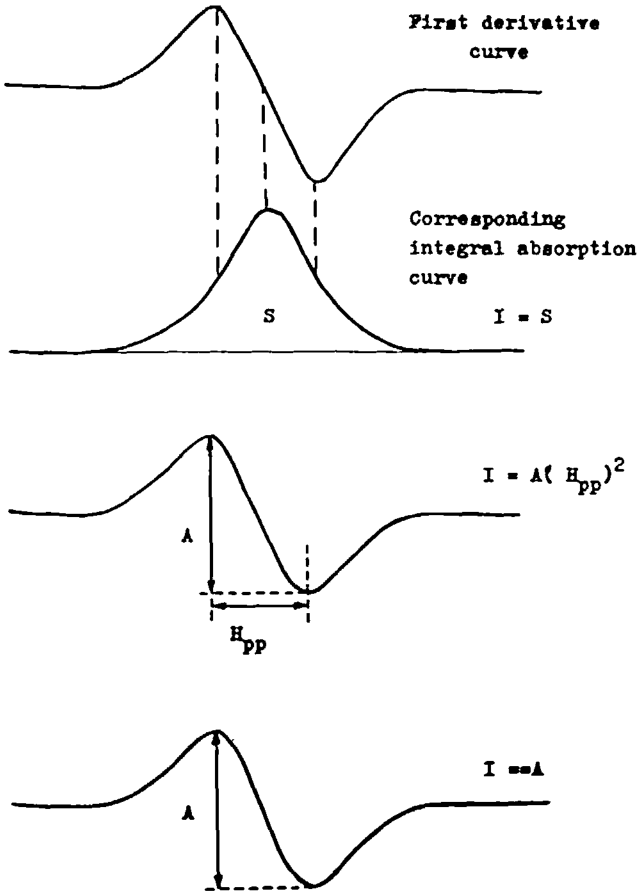


FIGURE 3. Possible measures of ESR signal intensities. (a) Double integral of the experimental spectrum (S) (general case); (b) the product of amplitude (A) and the square distance between the points of maximum slope of the integral curve (ΔH_{pp}) (the form of the line is constant); (c) the amplitude of the first derivative curve (the form and the width of the line are constant).

sure that the linewidth really remains constant within the other experimental errors in the conditions of analysis. The lineshape can be changed, in particular, by paramagnetic metal ions or their complexes present in high concentration in the solution containing the radical to be determined,[296,297] by irreproducible degassing, and by some other factors. If the lineshape depends on the concentration of the radical to be determined, this difficulty can be easily overcome by using the calibration curve "concentration — first-derivative amplitude." But even in this case the analyst must be sure that the stock solutions and the solution to be analyzed differ only in the concentration of the radical to be determined. The problems associated with the quantitative determinations of concentrations in complicated conditions of changing lineshape are considered in the literature.[236,263]

III. METAL COMPLEXES WITH NITROXIDE-CONTAINING REAGENTS

Many of nitroxide-containing chelating reagents were studied in terms of complexing with metal ions; a number of spin-labeled complexes was obtained in the solid state and studied by means of various methods. For the reagents, whose structures were presented in the previous chapter, the references to the investigations of complexing ability and the properties of complexes are given in Tables 3 and 4. Besides, the studies of metal complexes of the following spin-labeled chelating reagents were reported: oxaminic acid (Cd, Co, Ni, Zn),[272] crown-ether with two radical groups (K),[271] semicarbazones (Co, Cr, Cu, Fe, Mn, Ni, Zn),[268,269,301] fluorine-containing enaminoketone (Co, Cu, Ni, Zn),[300,311] new Schiff base (Cu)[273] and other azomethinic reagents (Cu, Mn, Pd),[274,277,301,312] iminoamine (Co, Ni),[313] porphyrins (Ag, Cu, Fe, Mn, V),[215,218,314] dithiocarbamate (Au, Co, Cu, Fe, Hg, Ni, Pb, Pd, Zn),[284,315-317] and new xanthates (Ni).[307,308]

The compounds of this type also comprise numerous complexes obtained by attaching a spin label to the peripheral parts of the molecules of already synthesized metal chelates with diamagnetic ligands.[206-214,216,217,318-330] Related complexes — adducts of traditional diamagnetic-ligand metal chelates with spin-labeled monodenthate ligands — were also studied.[212,213,330-344] The compound of a similar type is the porphyrexid palladium complex.[218]

The spin-labeled reagents interact with metals almost in the same way as their more common diamagnetic analogs, i.e., the metal ion is usually coordinated by the donor atoms of the chelating group.

Generally speaking, the nitroxide itself also exhibits a certain coordinating ability, and in the absence of the other efficient complexing group in the molecule it can form complexes with metal ions.[221,223-232,334,345-349] However, the complexing ability of nitroxide is weak; thus, the values of monoadduct formation equilibrium constants of copper(II) hexafluoroacetylacetonate with di-*tert*-butylnitroxide and 2,2,6,6-tetramethylpiperidin-1-yloxy as low as $(4.2 \pm 1.9) \times 10^3$ and $(1.6 \pm 0.4) \times 10^3$, respectively, were reported.[223,332] Therefore, the nitroxide group cannot compete in binding metal ions even with "the weakest" chelating groups. Being rather remote from the donor atoms of the reagent molecule, it does not usually participate in the coordination of metals. In solutions with high chelate concentrations, or in a solid-state intermolecular coordination of a peripheral nitroxide group of one chelate molecule into the vacant position of the central metal ion coordination sphere of another molecule may, however, exist. Such coordination was observed or proposed in a number of works.[88,273,304,332,337,350]

Numerous studies on the chelates of various nitroxide-containing reagents have shown that these compounds are quite analogous to the chelates of diamagnetic reagents of the corresponding class with respect to their composition, structure, solubility, extraction, and some spectral properties.[219,222] This situation is important for analytical applications, since it permits one to estimate *a priori* the usefulness of the new or even not yet synthesized spin-labeled chelating compounds to be applied as reagents.

However, the nitroxide-containing chelates essentially differ from their diamagnetic analogs with respect to their magnetic susceptibility and ESR-spectroscopic properties. Of special importance for the development of analytical methods are the ESR-spectroscopic properties.

As a rule, in the process of binding the metal ion, the nitroxide-containing reagent does not lose its ability to produce the ESR spectrum, however, the spectrum shape of the complex obtained can vary.

The ESR spectra of some chelates (of few ones) are obviously the same as the spectra of the initial radical-containing reagents, i.e., they appear to be triplets in solution. These are, for example, the chelate spectra of zinc(II) (Figure 4a), cobalt(III), nickel(II), and thallium(I) with xanthate 93;[99] cadmium(II), zinc(II), cobalt(II), and nickel(II) with aminodiacetic acid 57,[82] and others. The coincidence of the ESR spectrum of the

Table 3
NITROXIDE-CONTAINING CHELATING REAGENTS STUDIED WITH RESPECT TO THEIR COMPLEXING WITH METALS

Reagent	Metals	Ref.
1	Cu(II), Fe(III), Hg(II)	170—172
2	Co(II), Cu(II), Eu(III)	50, 171, 172
8	Co(II), Cu(II), Eu(III), Mn(II), Ni(II), Pr(III)	51
9	Co(II),Cu(II), Eu(III), Mn(II), Ni(II), Pr(III)	51, 52
10	Co(II), Cu(II)	52
12	Cu(II)	54, 173, 174, 304
13	Cu(II)	55, 305
14	Cu(II)	55, 175, 305
15	Cu(II)	59
16	Co(II), Cu(II), Ni(II), Pd(II)	176—178
17	Co(II), Cu(II), Ni(II), Pd(II)	176—179
18	Cu(II)	59
25	Cu(II)	59
26	Cu(II)	59
27	Co(II), Cu(II), Eu(III), Ni(II), Pr(III), Zn(II)	180
30	Ni(II)	64
31	Ni(II)	64
32	Co(II), Cu(II), Ni(II)	64
47	Cd(II), Co(II), Cu(II), Fe(III), Mn(II), Ni(II), Zn(II)	181
48	K(I), Na(I)	75
50	Co(II), Cu(II), Ni(II), Pd(II), Zn(II)	77, 182, 300
51	Co(II), Cu(II), Ni(II), Pd(II), Pt(II), Zn(II)	78, 94
55	Co(II), Cr(III), Cu(II), Ni(II), Pd(II), Zn(II)	80, 180, 183, 301, 303
57	Cd(II), Co(II), Cu(II), Ni(II), Zn(II)	82
58	Co(III), Cu(II), Ni(II), Pd(II)	184, 185
60	Co(II,III), Cu(II), Fe(III), Ni(II), Pd(II), Zn(II)	84, 86, 96, 176, 187—189
61	Cu(II)	85, 190
63	Co(III), Cu(II), Ni(II)	86, 87, 191
64	Co(III), Cu(II)	86
66	Co(II), Cu(II), Fe(III), Ni(II)	84, 302
67	Cu(II)	88, 302
68	Cu(II)	88, 192, 193, 302
69	Cu(II)	88, 302
70	Cu(II)	85
71	Cu(II)	88
72	Cu(II)	87
76	Co(II), Cu(II), Hg(II), Pd(II)	89, 194
77	Ag(I), Cu(II), Li(I), Rh(III)	186, 299
78	Li(I)	299
80	Co(III), Cu(II), Ni(II), Pd(II), Pt(II)	185, 195, 220, 303
81	Co(III), Cu(II), Ni(II), Pd(II)	196, 197, 303
82	Ag(I), Cd(II), Hg(II), Pb(II), Zn(II)	90, 93
83	Ag(I), Cd(II), Hg(II), Pb(II), Zn(II)	90
85	Co(II), Cu(II), Pd(II), Pt(II), Zn(II)	94, 176
88	Cu(II), Ni(II), Pt(II), Zn(II)	96, 176
89	Cd(II), Cu(II), Fe(II), Ni(II), Pd(II), Pt(II), Zn(II)	198, 301
92	Ag(I), Au(I,III), Cd(II), Co(II,III), Cu(I), Hg(II), Mn(II), Ni(II), Pb(II), Pd(II), Rh(III), Ru(IV), Tl(I), Zn(II)	53, 98, 199—202, 306—309
93	Co(III), Ni(II), Tl(I)	99
94	Hg(II), Pd(II), Tl(I)	203, 204, 303, 310
95	Hg(II)	205

Table 4
NITROXIDE-CONTAINING CHELATES ISOLATED IN SOLID STATE (A — REAGENT ANION)

Reagent	Complexes	Ref.
1	CuA_2	171, 172
2	CoA_2, CuA_2, EuA_3	50, 171, 172
8	CoA_2, CuA_2, EuA_3, MnA_2, NiA_2, PrA_3	51
9	CoA_2, CuA_2, EuA_3, MnA_2, NiA_2, PrA_3	51, 52
10	CoA_2, CuA_2	52
12	CuA_2	54, 173, 174, 304
13	CuA_2	55, 305
14	CuA_2, $^{63}CuA_2$	55, 175, 305
15	$CuA_2 \cdot H_2O$	59
16	CoA_2, $CuA_2 \cdot H_2O$, CuA_2Py_2, $(CuA_2 \cdot EtOH)_2$, $Ni_2A_4(HA)_2(H_2O)$, $Pd_3A_4(HA)_2Cl_2$	176—178
17	CoA_2, CuA_2, $CuA_2 \cdot H_2O$, $(CuA_2 \cdot EtOH)_2$, $Ni_2A_4(HA)_2(H_2O)$, $Pd_3A_4Cl_2(H_2O)_2$	176—179
18	$CuA_2 \cdot H_2O$	59
25	$CuA_2 \cdot H_2O$	59
26	$CuA_2 \cdot H_2O$	59
27	$CoA_2 \cdot 2H_2O$, $CuA_2 \cdot H_2O$, $EuA_3 \cdot 2H_2O$, $NiA_2 \cdot 2H_2O$, $PrA_3 \cdot 3H_2O$, $ZnA_2 \cdot 2H_2O$	180
30	NiA_2	64
31	NiA_2	64
32	CoA_2, CuA_2, NiA_2	64
47	CdA_2, CoA_2, CuA_2, FeA_3, MnA_2, NiA_2, ZnA_2	181
50	CoA_2, CuA_2, NiA_2, NiA_2Im_2, NiA_2Py_2, NiA_2Pz_2, NiA_2Phen, PdA_2, ZnA_2	77, 300
51	CoA_2, CuA_2, $CuA_2 \cdot 2H_2O$, $NiA_2 \cdot 2H_2O$, PdA_2, $PtA_2 \cdot 2H_2O$, ZnA_2	78, 94
55	$CoA_2 \cdot 4H_2O$, $CrA_2Cl \cdot H_2O$, $CuA_2 \cdot 4H_2O$, $NiA_2 \cdot 2H_2O$, PdA_2, ZnA_2, $ZnA_2 \cdot 4H_2O$	80, 180, 183, 301, 303
57	$CdACH_3COOH$, $CoACH_3COOH$, $CuACH_3COOH$, $NiACH_3COOH$, $ZnACH_3COOH$	82
58	$CoA_3 \cdot H_2O$, $CuA_2 \cdot 2H_2O$, $CuACH_3COO \cdot H_2O$, $NiA_2 \cdot 2H_2O$, $PdA_2 \cdot 2H_2O$	184, 185
60	CoA_2, CoA_3, CuA_2, NiA_2, PdA_2, ZnA_2	84, 86, 96, 176, 187—189
61	CuA_2, $CuA_2 \cdot CH_3C(O)CH_3$	85, 190
63	CoA_3, CuA_2, NiA_2	86, 87, 191
64	CoA_3, CuA_2	86
66	CuA_2	84, 302
67	CuA_2	88, 302
68	$(CuA)_2$, $CuACl$, $CuA \cdot HCl$, $CuA_2 \cdot Py$	88, 192, 193, 302
69	$(CuA)_2$	88, 302
70	$CuA_2 \cdot CH_3C(O)CH_3$	85
71	$(CuA)_2$	88
72	$(CuA)_2$	87
77	AgA_2BF_4, $CuACl(CO) \cdot H_2O$, $Rh_2Cl_6A \cdot 3H_2O$ (A — reagent molecule)	186
80	$CoA_3 \cdot H_2O$, $CuA_2 \cdot 2H_2O$, $NiA_2 \cdot 2H_2O$, $Ni(HA)_2Cl_2$, $NiACH_3COO \cdot H_2O$, PdA_2, PtA_2	185, 195, 303
81	$CoA_3 \cdot H_2O$, $CuA_2 \cdot 2H_2O$, $NiA_2 \cdot 2H_2O$, PdA_2, $(PdACl)_2$, $(PdABr)_2$	196, 197, 303
85	$CoAI_2$, $(CuACl)_2$, $PdACl_2$, $PtACl_2(H_2O)_2$, $ZnACl_2$ (A — reagent molecule)	94, 176
88	CuA_2, NiA_2, $NiA_2 \cdot 2H_2O$, PtA_2, ZnA_2	96, 176
89	$CuACl \cdot H_2O$, CdA_2, FeA_2, NiA_2, PdA_2, PtA_2, ZnA_2	198, 301
92	AgA, AuA, CdA_2, CoA_3, $CophenA_2$, $CuA \cdot H_2O$, HgA_2, $MnphenA_2$, NiA_2, $NiphenA_2$, PbA_2, PdA_2, RhA_3, RuA_4, TlA, ZnA_2, $ZnphenA_2$	98, 199, 201, 202, 307—309
93	CoA_3, NiA_2, TlA	99
94	$HgACl$, $HgAC_3H_7COO$, $(PdACl)_2$, $(PdABr)_2$, $(PdAI)_2$, $TlACl_2$, TlA_2Cl, $TlA(OCOC_3H_7)_2$, $TlA_2OCOC_3H_7$	203, 204, 303, 310
95	HgA_2	205

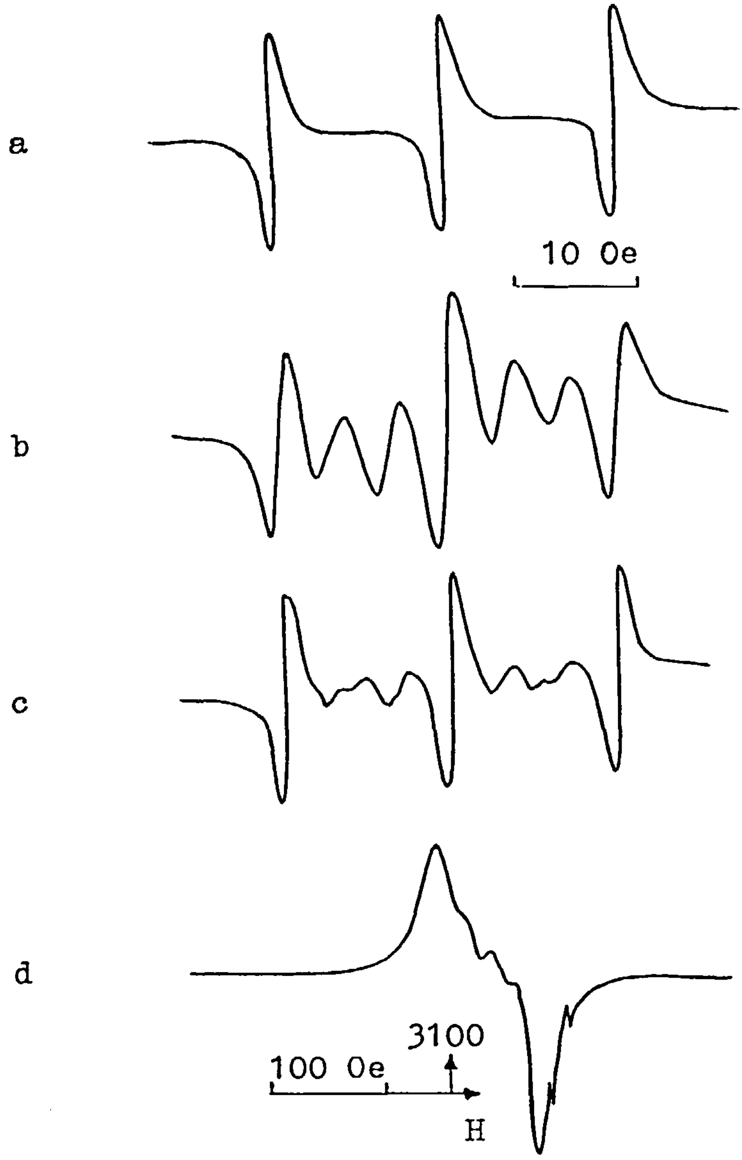


FIGURE 4. The room-temperature ESR spectra of the solutions of nitroxide-containing chelates. (a) The complex of zinc(II) with xanthate 93 (X-band, 1×10^{-4} *M* in chloroform, microwave power 20 mW, modulation amplitude 0.1 Oe); (b) the complex of cobalt(III) with the Schiff base 60 (X-band, 5×10^{-4} *M* in deoxygenated toluene); (c) the complex of zinc(II) with the Schiff base 60 (X-band, 5×10^{-4} *M* in deoxygenated toluene; (d) the complex of copper(II) with the Schiff base 60 (X-band, 5×10^{-4} *M* in THF); the interpretation of this spectrum is given by Eaton and Eaton.[187]

complex compound molecule carrying two or three nitroxide groups (and sometimes, also, a paramagnetic metal ion) with the spectrum of the monoradical reagent indicates that the paramagnetic centers of such chelates interact so weakly as not to be observed. However, it is more often when the paramagnetic centers in the chelate molecule do interact appreciably and the ESR spectrum of the complex compound solution somehow differs from that of the original reagent solution.

The nitroxide-containing complexes of *diamagnetic* metal ions are essentially nitroxide bi- or triradicals, the only difference being the composition of the chain (combining the nitroxide groups in their molecules) which contains the metal atom. The ESR spectra of such compounds are usually similar to those of organic nitroxide bi- and polyradicals and, thus, can consist of five, seven, and more numbers of lines symmetrical with respect to the spectrum center, e.g., chelate spectra of cobalt(III) and zinc(II) with Schiff base 60 (Figure 4b and c),[189] palladium(II) with iminooxime 80,[185] and many others. Very often the relative intensity of the lines in ESR spectra of such chelates, and sometimes their number, depend on temperature and nature of the solvent. For example, the spectrum of zinc(II) and Schiff base 60 complex in tetrahydrofuran consists of nine lines (Figure 4b), while in toluene it becomes an ordinary triplet.[189]

Along with the unpaired electrons of nitroxide groups, the molecules of chelates of *paramagnetic* metal ions contain the unpaired electrons of *d*- or *f*-orbital of the metal and the ESR spectrum is defined by the totality of interactions in the system of nonequivalent unpaired electrons. In some complexes these spin-spin interactions are very weak, and the ESR spectrum consists of the superposition of lines (sometimes slightly broadened) typical of free nitroxide radical and paramagnetic metal ion in the appropriate coordination (provided relaxation process does not "smooth out" metal signal). Such spectra were reported for porphyrin complexes of copper(II)[216] and vanadium(IV).[314]

But in most cases spin-spin interactions change the ESR signals of both the metal ion and nitroxide radicals. For paramagnetic metal ions with slow electron spin relaxation rates, such as Cu(II), V(IV), and Hg(II), electron-electron spin-spin interactions result in the splitting of the allowed transitions in the spectra. The spectral lines of the two types of paramagnetic centers of the molecule become changed to more or less extent, depending on mutual superposition and degree of broadening of multiple lines resulted from splitting. One of such spectra is shown in Figure 4d. Spin-spin interactions sometimes lead to very complicated spectra, where "metal" and "nitroxide" lines cannot be readily found. The shapes of such spectra can be understood on the basis of computer simulation only.

In the case of spin-labeled complexes of paramagnetic metal ions with rapid electron spin relaxation rates, the ESR spectra of metals cannot be easily observed and splittings of the ESR signal of a nitroxide radical due to interaction with the metal is collapsed by the metal relaxation.[297]

ESR spectra of some nitroxide-containing paramagnetic ion complexes with very strong spin-spin interactions failed to be detected at all.[184,195]

The theoretical background of interpretation of ESR spectra of paramagnetic metal ion spin-labeled complexes and the description of the algorithm of the program for computer simulation of such spectra can be found in the literature.[208,211,351,352] Eaton and co-workers performed a large series of experimental investigations with quantitative interpretation of ESR spectra of nitroxide-containing complexes with copper(II),[178,206,207,209-216,318-320,323-325,330-336,339] vanadium(IV),[314,321,334,335,336,339] silver(II),[314,322,326] manganese(II,III),[274,278,338] nickel(II),[307,308] cobalt(II),[337] and iron(III).[327] These complexes contain only one nitroxide group per molecule in most cases, but, nevertheless, they can serve as valuable simplified models of real chelates used for metal determination.

The information about the dependence of the ESR spectrum of the chelate on its composition and structure is of special interest for the analysts dealing with the development of methods for the determination of metals with the aid of nitroxide-containing reagents. In fact, the possibility of ESR-spectroscopic measurement of the complex concentration in the presence of the reagent, which is always taken in excess, will depend upon the changes in the ESR spectrum of the radical-containing molecule after binding the metal ion. The dependence of the direction and the degree of such a change upon the nature of the metal will determine to a considerable extent the selectivity of the analytical method.

Unfortunately, no theory capable of predicting the ESR spectra of spin-labeled complexes on the basis of their structure, as well as of evaluating the range of their changes, has been developed yet, though in recent years many systematic investigations have been performed (see publications of Eaton cited above). It was experimentally shown that spin-spin interactions and, consequently, the ESR spectrum of a chelate depend on such structural factors as the size and the type of nitroxide-containing heterocycle,[214,318,327,333,335,337] the nature of atoms and bonds in the chain between paramagnetic centers of the molecule,[207,211,214,216,308,318,319,335-338] chain *cis-trans* isomerization,[210,214,318,322] molecule conformations,[215,325,330] nature of substituents in ligands,[211,323] mutual position of substituents in aromatic fragments,[216,322,333,335,337] the presence of additional methylene groups in the chain,[214,216,327,333,336] the nature of metal ion,[307,314,322] and the nature of the solvent.[172,209,211,214-216,314,323,326,327] The multiplicity of *the interrelated factors cited makes it difficult to deduce inambiguous recommendations* suitable in practice.

Nevertheless, vast empirical material available suggests that a great majority of the nitroxide-containing complexes of various metals possess ESR spectra which consist of narrow and intensive lines similar to those of the ESR spectra of the original reagents. Of course, the presence of metal ion broadens to some extent the spectral lines of nitroxide radicals. The broadening results from the change in molecule tumbling rate by metal binding and from intramolecular spin-spin interactions. But, at least for diamagnetic ion complexes, the broadening is not great and rarely exceeds several oersted. The general situation for paramagnetic ion chelates is not quite clear at present, but, at least for *some paramagnetic metal ions, nitroxide-containing complexes with nar*row-line ESR spectra are known. It makes the method rather universal for the determination of metals through spin-labeled compounds and the dependence of the detection limits upon the nature of the element to be determined weak. On the other hand, the ESR spectra of many chelates of various metals considerably differ from the ESR spectra of the original reagents. It gives a new perspective for the determination of the complexes' concentrations without separating them from the excessive reagent, at least in those cases when the excess required is not very large.

IV. APPLICATION OF NITROXIDE-CONTAINING CHELATING REAGENTS FOR THE DETERMINATION OF METALS

Wide and increasingly great variety of already synthesized spin-labeled nitroxide chelating reagents, high stability of nitroxide radicals in real conditions of analytical operations, the ability of nitroxide-containing compounds to form chelates with many metals without losing unpaired electrons, narrow linewidth in the ESR spectra of such complexes — all these facts create favorable conditions for the development of the methods for the determination of metals based on the ESR spectrometry of their radical-containing complexes.

Such determination seems to require the following operations: first, to bind quantitatively the metal with the appropriate spin-labeled reagent to form a complex; second, to record the ESR signal of this complex (and to separate it from the signals of other radical-containing components of the system, first of all of the excessive reagent); third, to measure the intensity of this signal with high sensitivity, accuracy, and precision; and, finally, to determine the concentration of the metal bound by the intensity measured.

Since the solutions in nonpolar solvents are most favorable for highly sensitive ESR-spectroscopic measurements,[353,354] the most convenient technique for binding the metal in a spin-labeled complex appears to be extraction of the metal from aqueous into nonpolar organic solvent media containing a spin-labeled reagent. Successful development of this aspect of the method of spin-labeled reagents has been promoted by a high level of theoretical development of the extraction of chelates.[233,234]

The problem of isolating the ESR signal of the metal chelate being determined from the signals of other nitroxide-containing components of the system (such as the excessive reagent, chelates of other metals) can be solved either by ESR-spectroscopic techniques (resolution ability of the spectrometer) or by means of preliminary separation of the chelate in question from all the other spin-labeled compounds using chemical or physicochemical methods, e.g., extraction or chromatography. In case of solving the problem using the second approach, of interest can be experience gained upon the determination of metals with the aid of a complexing reagent containing a radioactive label.[235]

It is quite clear that the proper choice of the optimal conditions for quantitative extraction of a metal, as well as the best way of isolating the signal of its chelate, requires a preliminary systematic investigation of the properties of both the reagent itself and the chelates of the metal to be determined and the other accompanying metals.

A highly sensitive ESR spectrometer and correct procedure of spectrometry are the necessary factors for the determination of the ESR spectrum intensity with a sufficient detection limit, accuracy, and precision.

The best modern ESR spectrometers are capable of recording signals of nitroxide radicals in concentrations *circa* 10^{-9} *M*, provided dielectric losses in solution are small.

Methodological aspects of quantitative determination of concentrations constitute a little more complicated problem in ESR spectrometry than in most other spectroscopic analytical methods, since many factors influence the magnitude of the ESR signal. For many years the techniques of determining the intensities of ESR spectra were given little attention, which resulted in large inaccuracies.

The methodology of quantitative ESR determinations is a rather broad field of knowledge which cannot be covered thoroughly in one chapter of a review. On the other hand, the determination of metals with nitroxide radicals has little or no special methodological points differing from general recommendations. Therefore, we shall not not discuss these problems here and refer the reader to special literature.[1,236-238,263,353-362]

It has been demonstrated that well above the detection limit the relative intensity measurement error can be readily decreased to 1 to 3%.

The fourth problem, that is, determination of the metal concentration according to the spectral intensity measured, can be solved with the aid of the method of the calibration plot based on the results of the analyses of the reference samples, which included all the operations of the determination techniques.

Now we consider the published works devoted to the development of the method of the determination of metals with nitroxide-containing reagents. Since the development of analytical procedures is based upon the investigation of a number of general properties of the reagent being used, it is convenient to classify the material published according to spin-labeled compounds used. Besides, such an approach is favorable for the systematization of the techniques for isolating the ESR signal of the metal complex being determined, as well as the clarification of the peculiarities of the spin-labeled compounds considered as a subclass of analytical chelating reagents.

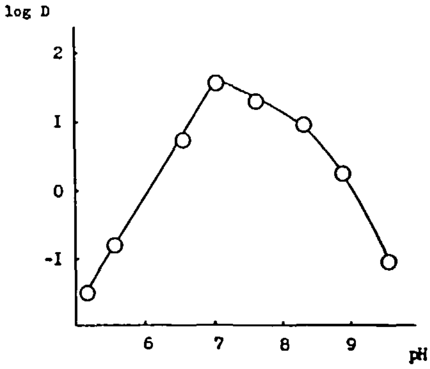


FIGURE 5. Extraction of zinc(II) with xanthate 92 depending on pH of the aqueous phase. Zinc concentration is 10^{-4} *M*; reagent concentration is 10^{-3} *M*.

So far, the following five nitroxide-containing chelating reagents have been investigated by analysts: β-diketone 1, hydroxyimine 50, oxyazocompound 76, iminooxime 80, and xanthate 92.

It should be noted that the first investigations were performed with ESR spectrometers which cannot be regarded as modern and sensitive. Thus, the detection limits for nitroxide radicals in nondegassed chloroform solution amount to 1×10^{-5} *M* for the EPA-2M spectrometer and 1×10^{-7} *M* for the RE-1306 spectrometer. Therefore, the detection limits given for metals do not represent all the possibilities of the method considered. The reader should remember as well that in most of these investigations model aqueous metal solutions were used. These solutions did not contain other metals or complexing reagents except for the cases specially defined.

A. Xanthate

Nitroxide-containing potassium xanthate 92 is a yellow solid substance. It is readily soluble in both organic solvents and water. The acidic dissociation constant of the chelating group of this compound (—C(S)SH) is rather high: pK_a equals 5.4 at the ionic strength 0.1 (sodium perchlorate).[53] Such a considerable ability to dissociate results in a situation when, upon the equilibrium of the chloroform phase and the aqueous solutions of the reagent at pH more than 6 (by extraction of metals, in particular), the spin-labeled xanthate is practically completely found in the aqueous phase in the form of anion.

The radical-containing xanthate is capable of extracting iron, cobalt, copper, nickel, mercury, silver, zinc,[53,200] and probably some other elements from the aqueous solution into chloroform. The methods of isomolar series[200] and equilibrium shift[53] suggest that the metals are extracted in the form AgA, HgA_2, ZnA_2 complexes (A is the reagent anion). The completeness of extraction was investigated quantitatively only in the case of zinc (Figure 5): under optimal conditions (at pH 7, a tenfold excess of xanthate and equal volumes of the phases) the metal is recovered to 96%.[53] Palladium is extracted best from the acetate solution at pH 6, and silver and mercury are well extracted from the ammonium solution at pH 10.[200]

The ability of the xanthate to extract metals effectively from neutral and alkali media and, at the same time, quantitatively remain in the aqueous phase made it possible to develop a number of procedures for the determination of metals based on the extractive separation of their spin-labeled xanthates from the excessive reagent.

Thus, the method for the determination of zinc[53] comprises extraction of the metal into chloroform under optimal conditions (pH 7, a tenfold excess of the reagent). The spin-labeled chelate ZnA_2 formed is quantitatively extracted into the organic phase, while the excessive reagent is not extracted into chloroform at all under the same conditions. Therefore, its signal does not hinder the determination of the concentration of the zinc chelate, whose ESR spectrum coincides with that of xanthate completely (Figure 3a). The authors of the method have suggested to use as a measure of zinc concentration the product of the amplitude of the resulting organic phase ESR spectrum derivative and the line halfwidth squared. When the spectra are recorded on the Varian-4502 ESR spectrometer, the detection limit 6×10^{-8} g-ion/l is attained.

Palladium can be extracted into chloroform from an acetate buffer solution at pH 6 in the presence of about a 20-fold excess of the spin-labeled reagent.[200] The spectrum of palladium xanthate is also an ordinary triplet. The concentration of this compound can be measured by the ESR method owing to the fact that, similar to the determination of zinc, the reagent itself completely passes into the aqueous phase in the process of metal extraction. The concentration of palladium is determined using a calibration plot. Using an EPA-2M ESR spectrometer of low sensitivity the authors could determine microgram quantities of palladium in the catalysts ($\sim 10^{-3}\%$).[200] The relative standard deviation was equal to a few percent.

Similar methods have been developed for determination of silver and mercury. The metal being determined is extracted into chloroform from the ammonium solution (pH 10) in the presence of a tenfold excess of xanthate and a great excess of the tartrate ions to prevent the metal hydrolysis. The ESR spectra of the extracting complexes of these metals are also triplets: the metal concentration is determined from the intensity of these spectra using the calibration plots.[200] The method was applied for the determination of microgram quantities of mercury in stupp and silver in zinc concentrate; the relative standard deviation of the results was less than 0.05.

Also, a more complicated method using xanthate 92 for the determination of copper is described, which seems to be based upon the redox reaction of copper(II) with the xanthate group of the reagent,[239-241] though no reliable proofs of this mechanism are given. The detection limit on the EPA-2M is 1×10^{-5} g-ion/l; relative standard deviation is 0.07.

Thus, the use of the spin-labeled xanthate makes it possible to determine a number of diamagnetic metal ions forming stable complexes with sulfur-containing reagents by the ESR method. By using this compound we demonstrated the procedure of complete extraction separation of the spin-labeled chelate of the metal from the excessive spin-labeled reagent. The separation desired proceeds within one stage along with the metal extraction and no special efforts are required from the analyst. Unfortunately, the possibility of using this simple procedure is confined by the reagents with a high dissociation constant and not very high distribution constant. In fact, xanthate 92 remains the only investigated compound so far meeting these requirements.

B. β-Diketone

β-Diketone 1 with a spin-label in the form of imidazoline (IX) derivative is readily soluble in nonpolar organic solvents and aqueous alkali solutions. The presence of the imine nitrogen atom in the radical-containing heterocycle makes possible the existence of two charged forms of this compound in addition to the electroneutral one: protonated at the nitrogen atom at position 3 of the heterocycle ($pK_a = 2.02$; $\mu = 0.1$, $NaClO_4$) and the form with a dissociated β-dicarbonyl group ($pK_a = 6.45$; $\mu = 0.1$, $NaClO_4$).[170,244]

The unusually high value of the β-diketone dissociation constant of the chelating group is indicative of a strong electron-acceptor effect of the spin-labeled heterocycle.

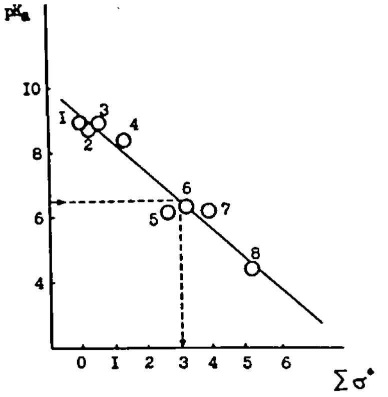


FIGURE 6. Dependence of the dissociation constants of β-diketones upon the sums of the Taft constants of substituents: (1) acetylacetone; (2) furoylacetone; (3) benzoylacetone; (4) thenoylacetone; (5) trifluoroacetylacetone; (6) benzoyltrifluoroacetone; (7) thenoyltrifluoroacetone; (8) hexafluoroacetylacetone. (The process of the determination of ($\sigma^*_{CH_3} + \sigma^*_R$) is shown with an arrow.)

Estimation by means of β-diketone correlation dependence of pK_a values on the sums of the substituent Taft constants (Figure 6) resulted in the σ^* value for this fragment equal to 3.0.[245] The same result is attained in a similar treatment of pK_a value for fluoro-containing spin-labeled β-diketone 2 ($pK_a = 4.66$).[245] Experimental data[246] and the analysis of impacts of atoms constituting the heterocycle into its total electronegativity, performed by group electronegativities method of Hinze,[366-368] led to the conclusion that such a high electronegativity of the cycle is due to the presence of the unpaired electron.[247,365]

The distribution ratio of β-diketone 1 in the system chloroform-water determined spectrophotometrically is rather high: $\log K_D = 3.34$. This value corresponds to the values of distribution ratios of diamagnetic β-diketones of close molar volumes, e.g., benzoylacetone ($\log K_D = 3.44$); this closeness indicates that the introduction of the unpaired electron into the molecule of the organic substance does not substantially affect its behavior in the two-phase system, which remains to be well described in terms of the theory of regular solutions.[248] The contribution made by the radical-containing 2,5-dihydro-2,2,5,5-tetramethyl-1H-imidazol-1-yloxy substituent present in the spin-labeled β-diketone 1 to the molar volume of the compound was determined (Figure 7): $V = 82$ cm^3.[247] On the basis of the correlations similar to that shown in Figure 7 and knowledge of the estimates of V, it is possible to predict any changes in the distribution ratios of the reagents resulting from the introduction of the spin label into their molecules.

Though the acid dissociation constant of β-diketone 1 is sufficiently high, it appeared to be possible to quantitatively extract this compound from chloroform back into the aqueous phase only after pH was raised to 11 (Figure 8), which was due to a high distribution ratio.[170,247]

A review of the investigation of the extracting ability of the spin-labeled β-diketone performed by reverse-phase paper partition chromatography has shown that the most complete extraction into chloroform with the use of this reagent is obtained for copper, mercury, erbium, lead, cadmium, and, in the presence of caproic acid, iron(III).[170] Extraction of copper, mercury, and iron was studied in more detail by using extractive procedures and radioactive indicators; dependences of the distribution ratios of these

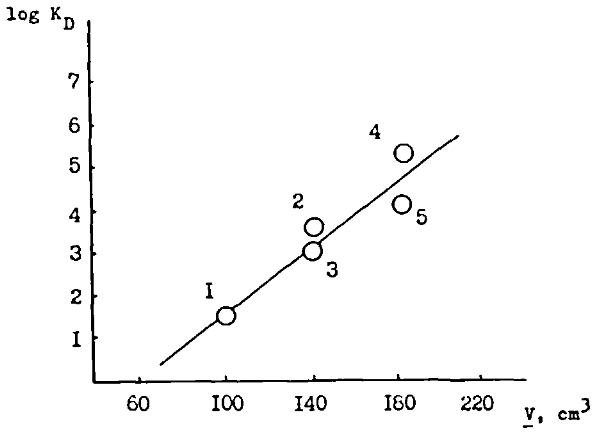


FIGURE 7. Dependence of distribution constants of β-diketones in the chloroform-water system upon the values of molar volume: (1) acetylacetone; (2) benzoylacetone; (3) selenoylacetone; (4) dibenzoylmethane; (5) benzoylselenoylmethane.

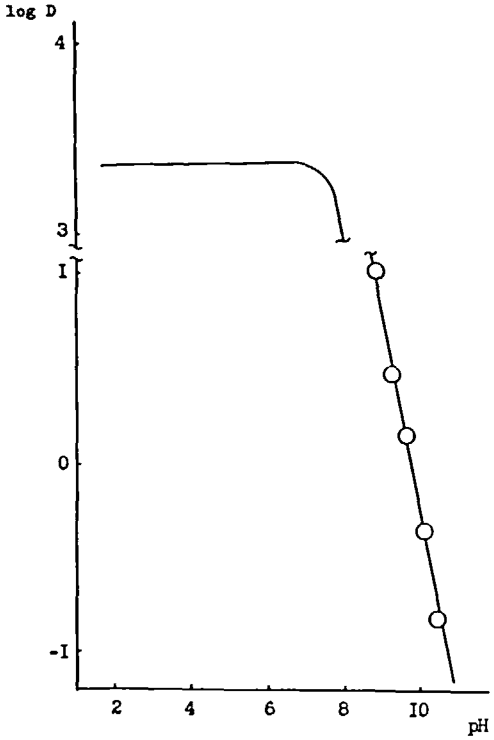


FIGURE 8. Dependence of distribution ratio of β-diketone 1 in the chloroform-water system on pH (μ = 0.1, $NaClO_4$; reagent concentration 5×10^{-3} *M*).

metals on pH are presented in Figure 9.[170] Under certain conditions these three metals can be extracted into chloroform quantitatively, however, the extraction of mercury and iron proceeds slowly: it takes 1 to 3 hr to attain equilibrium in these systems, probably due to hydrolytic process hindrances.

Regularities of extraction suggest that copper is extracted in the form of the ordinary chelate CuA_2 (A is the anion of the spin-labeled β-diketone), iron is extracted as a

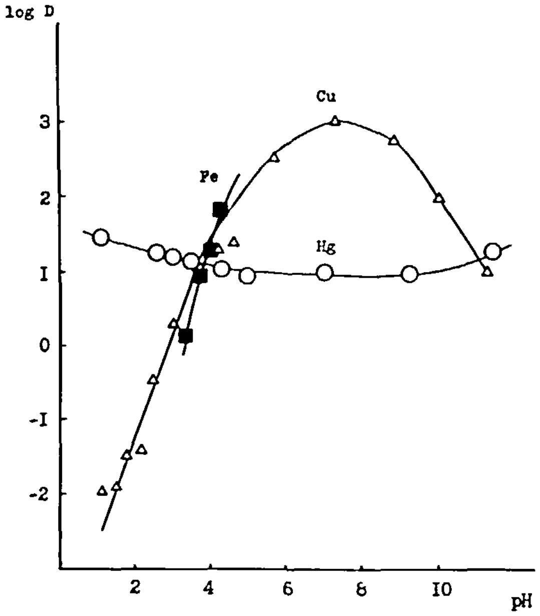


FIGURE 9. Extraction of copper (△), iron (■), and mercury (○) with β-diketone 1 depending on pH. Concentrations: copper — 5 × 10^{-4} *M;* iron — 10^{-5} *M;* mercury — 10^{-4} *M;* β-diketone: △, ○ — 5 × 10^{-2} *M*, ■ — 2 × 10^{-2} *M;* caproic acid (■) — 10^{-2} *M;* sodium perchlorate — 0.1 *M*.

mixed complex with β-diketone 1 and caproate ion, and mercury is apparently in the form of organometal compound with the bond between the mercury atom and the intercarbonyl carbon atom of the β-diketone group.[170,247]

The consideration of the stability constant of the copper(II) chelate, determined from the extraction equilibrium data, performed with the aid of correlation log β_2 = f(pK_a) suggested that the imine nitrogen atom of heterocycle does not participate in the metal coordination, as could be assumed, and copper(II) forms bonds with two oxygen atoms of the β-dicarbonyl group in the same way as with many other diamagnetic β-diketones.[170,247]

The dependence of the distribution ratio of mercury on pH, which is not quite typical of extraction of chelates and is probably observed due to extraction of organometal compound, was used for the development of the method of determining mercury with this β-diketone.[170] Sufficiently high values of the distribution ratios of mercury at pH 11 to 12, along with very low values of the distribution ratio of the reagent itself under these conditions, allow one to use an extraction version for the separation of the excessive reagent. However, a single-stage separation of the spin-labeled compound of mercury and the excessive reagent, similar to that applied for the determination of metals with xanthate, in this particular case is impossible, owing to mercury hydrolysis at pH 11. Therefore, the first stage of this procedure consists of metal extraction from the aqueous solution at pH 3 in the presence of 100- to 1000-fold excess of the reagent (β-diketone). The excessive reagent mainly distributing into the organic phase is removed by scrubbing the extract with alkali solution at pH 11. Then the extract which quantitatively retains the spin-labeled compound of mercury is used for recording the ESR spectrum. The intensity of the extract triplet spectrum being recorded (the first-derivative amplitude was used as a measure) is proportional to the mercury concentration

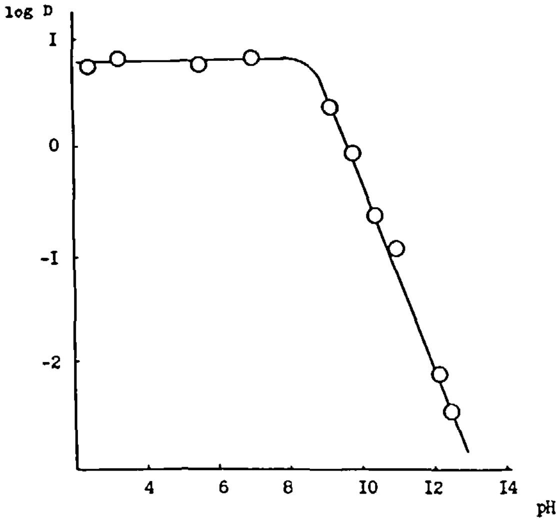


FIGURE 10. Dependence of distribution ratio of iminoxime 80 in the chloroform-water system on pH (μ = 0.1, $NaClO_4$; reagent concentration 5×10^{-3} *M*).

in aqueous solution before the extraction.[170] With the use of the Soviet-made ESR spectrometer RE-1306, the detection limit for mercury was found to be 1×10^{-7} g-ion/*l*; relative standard deviation of the determination of mercury well above the detection limit does not exceed 0.03 to 0.04.[247] Tenfold amounts of copper, iron(III), and lead do not affect the results of the determination; tenfold amounts of zinc, cadmium, and silver distort the results by 15 to 30%.

The determination of mercury is slightly hindered by the background ESR signal from the decomposition products of β-diketone, which also pass into the extract, however, careful purification of the reagent and the use of optimal procedures allow one to overcome these obstacles.[170,247]

Thus, the investigations of the nitroxide-containing β-diketone 1 have resulted in working out the method of the ESR-spectroscopic determination of the diamagnetic mercury with a rather good detection limit. They demonstrated once again the possibility of excluding the interfering effect of the excessive reagent signal by applying extraction procedures and made possible the quantitative description of the effect of the commonly distributed spin-label (imidazoline derivative) on the acidic properties of the chelating reagents and their distribution in two-phase systems.

C. Iminoxime

Oxime 80, possessing the same spin-label as β-diketone considered above and capable of forming chelates through coordinating the metal ions by the nitrogen atoms of the oxime group and the imidazoline cycle, appears to be a much weaker acid than the radical-containing xanthate and β-diketone: pK_a is 9.25 (μ = 0.1; $NaClO_4$). However, for the reagents of the oxime class this value is rather low, which confirms the conclusion about a high electronegativity of the spin-labeled substituent on the basis of imidazoline.[170,242] The distribution behavior of this reagent is shown in Figure 10.

The radical-containing iminoxime is capable of extracting palladium,[243] copper, cobalt, and nickel (Figure 11)[242] into chloroform; thus, with respect to selectivity this reagent resembles diamagnetic oximes. Extraction of palladium was not studied in detail; it was only found that the metal is extracted quantitatively as a chelate PdA_2 (A is the anion oxime) at pH 1.6 in the presence of the tenfold excess of the reagent.[243]

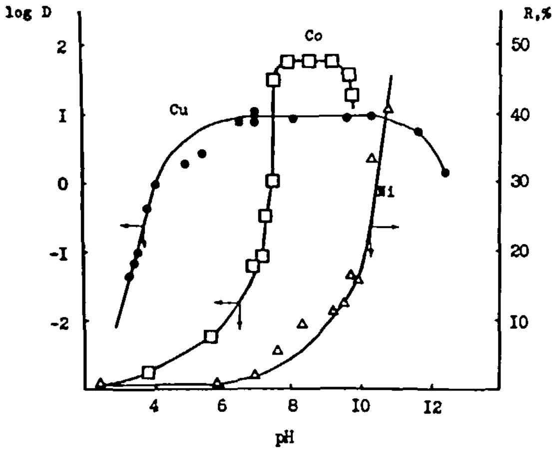


FIGURE 11. Extraction of copper (●), cobalt (□), and nickel (Δ) with iminoxime 80 into chloroform, depending on pH. Concentrations: copper and cobalt — 10^{-5} *M*; nickel — 10^{-4} *M*; reagent: (●) 5×10^{-3} *M*, (□) 10^{-3} *M*, (Δ) 10^{-2} *M*; sodium acetate (Δ) — 0.01 *M*.

Copper is extracted as the chelate CuA_2 ($\log \beta_2 = 15.8$), though not quite completely: the maximum extraction equals about 90%.

Cobalt is extracted quantitatively in the presence of the 100-fold excess of the reagent in the form of two nitroxide-containing complexes drastically differing in their chromatographic properties and ESR spectra (Figure 12). It is assumed that the compound with a quintet spectrum contains the metal in the trivalent state and has CoA_3 composition, as reported by Ovcharenko et al.[195]

The compound with a more complicated spectrum may be either the chelate of a paramagnetic cobalt(II) ion with considerable intramolecular spin-spin interactions or an adduct of this chelate with paramagnetic molecular oxygen, participating in the spin-spin interactions.[242,247]

Nickel can be extracted from the aqueous phase into chloroform quantitatively only after two successive extractions at pH 10.8 in the presence of the 500-fold excess of acetate ions, which prevent the hydrolysis of the metal. The extraction system reaches equilibrium after shaking for 30 min.[242]

The entirely extractive separation of the excessive reagent from chelates described above cannot be used in developing the procedures for the determination of metals with the oxime, due to the fact that the distribution ratio of this compound in the conditions of quantitative extraction is not sufficiently low and that the extraction of metals in the region of high pH, where the reagent completely passes into the aqueous phase, is not quite effective. This problem promoted the development of the two new techniques for detecting the chelate ESR signal.

The first technique was used in developing the method of the determination of palladium.[243] As has already been said, the chelate of this metal with the spin-labeled iminoxime is quite stable, so that the presence of only tenfold excess of reagent is required for its complete extraction into chloroform. On the other hand, the ESR spectrum of this chelate contains two lines which only slightly overlap the spectral lines of the reagent (Figure 13). After extracting palladium at pH 1.6 with the minimum excess of the reagent, it is possible, by making use of such a combination of the properties, to determine the chelate concentration in the extract (and, therefore, the metal concentration in the initial aqueous solution) according to the amplitudes of these lines without removing the unbound reagent which is present in the extract.

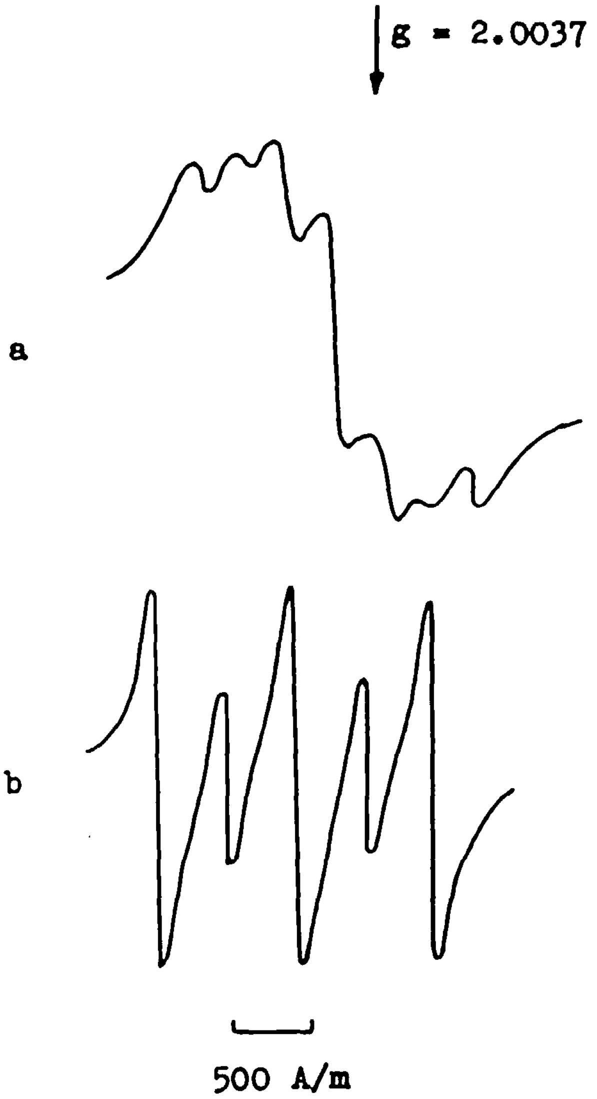


FIGURE 12. X-band ESR spectra of the extracting complexes of cobalt with iminoxime 80 in a chloroform (undeoxygenated) solution. (a) Dominating complex (97% of cobalt in extraction system); (b) admixed complex (room temperature, $\sim 5 \times 10^{-4}$ *M*, microwave power 5 mW, modulation amplitude 0.1 Oe).

The determination is performed with the aid of a calibration plot. The exact value of the detection limit of palladium is not known from the literature, however, it has been reported that by using the ESR spectrometer Varian E-3 it is possible to carry out the determinations within the concentration range of 5×10^{-6} to 4×10^{-5} g-ion/*l* with the relative standard deviation 0.05.[243]

The procedure used in this case is attractive due to the simplicity of performance. However, the area of its application does not seem very large. It requires a combination of a considerable difference between the chelate ESR spectrum and the reagent spectrum with a very high stability of the complex. Until recently the method of the determination of palladium described above remains the only example of its application.

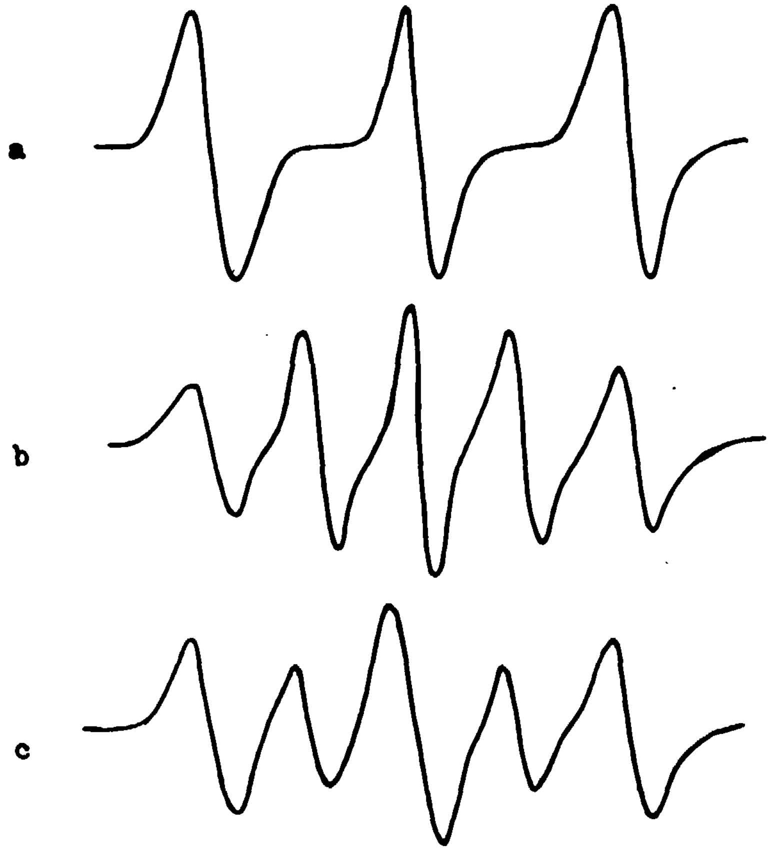


FIGURE 13. ESR spectra of chloroform (undeoxygenated) solutions of iminoxime 80 (a), chelate of this reagent with palladium(II) (b), and the extract containing both compounds (c) (X-band, room temperature; concentrations $\sim 10^{-4}$ *M*).

The spin-labeled oximates of cobalt do not possess the necessary stability. For this reason the determination of the metal without separation of the complex is impossible, despite a very substantial difference between their ESR spectra and the ESR spectrum of the reagent (Figure 12). Since extraction separation failed to reach the required results, the method of liquid chromatography was applied.

The method involves quantitative extraction of cobalt into chloroform at pH 9 and in the presence of a 100- to 1000-fold excess of the reagent with a succeeding chromatographic separation on a silica gel column (h = 75 mm; d = 6 mm), with the use of ethyl acetate-chloroform mixture in the ratio 1:2 as the mobile phase.[242] The excessive reagent which remained in the organic phase after extraction quantitatively leaves the column in the first portions of the eluate. In the following portions, the prevailing cobalt complex (the metal content is 97%) with a complicated ESR spectrum is eluated quantitatively (Figure 12a). The admixed complex containing no more than 3% cobalt remains in the upper part of the column. The measurement of the maximal amplitude of the complicated ESR spectrum of the eluate fraction with the dominating complex is a measure of cobalt concentration in the aqueous solution before extraction. The detection limit of the metal upon direct use of the eluate for recording the spectrum on the RE-1306 spectrometer is equal to 2×10^{-6} g-ion/*l*; if the eluate is evaporated and the remainder (cobalt chelate) is dissolved in chloroform exhibiting less dielectric losses, the detection limit decreases to 3×10^{-7} g-ion/*l*. The relative standard deviation

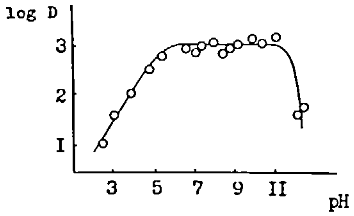


FIGURE 14. Distribution of oxyazocompound 76 in the chloroform-water system, depending on pH (μ = 0.1, $NaClO_4$).

in determining 10^{-5} g-ion/*l* of cobalt does not exceed 0.04. The results of the determination of cobalt are not affected by the presence of the tenfold amounts of nickel; the presence of copper in the same excess affect the results slightly, while iron(III) and lead more markedly interfere with the determination.

The procedure for the determination of nickel using this oxime also involves chromatographic isolation of the spin-labeled chelate from the extract obtained under optimal conditions.[242] However, in this particular case the isolation is reached much easier due to the fact that the spin-labeled nickel oximate is absorbed very effectively on silica gel. The extract is applied on a 2-mm silica gel layer covering the porous bottom of a glass funnel and the reagent excess is eluted by passing through this layer the chloroform-ethyl acetate mixture (1:2). The nickel chelate quantitatively remaining on the sorbent is then washed out with ethanol, which is a more effective effluent. Since ethanol as a solvent is not quite suitable for highly sensitive ESR-spectroscopic determinations, the procedure envolves its evaporation and dissolution of the chelate in chloroform. The amplitude of the ESR spectrum of the chelate chloroform solution, which is a usual triplet, is a measure of the nickel concentration in the aqueous phase prior to extraction. The relative standard deviation for the determination of nickel by this method is 0.15 to 0.20, which is rather high and seems to be due to incomplete dissolution in nonpolar chloroform of the wet chelate remaining after evaporation of ethanol. An increase in the relative standard deviation results in a greater detection limit, which amounts to 1 × 10^{-6} g-ion/*l* when recorded on the RE-1306 ESR spectrometer.

The development of the methods for the determination of cobalt and nickel has shown that simple chromatographic procedures make possible determinations with the aid of such spin-labeled reagents which do not exhibit prominent acidic properties and do not form the chelates with the ESR spectra markedly differing from the triplet; thus, the method described becomes universal with respect to the nature of the reagent through the use of chromatography.

D. Oxyazocompound [89,194]

The spin-labeled oxyazocompound 76, similarly to oxime 80, is a very weak acid; pK_a amounts to 10.94 ($\mu = 0.1$, $NaClO_4$). This property, along with a high distribution ratio in the chloroform-water system ($\log K_D = 2.94$), makes the reagent predominantly be in the organic phase even by highly alkaline solutions (Figure 14).

The investigations by the method of partition reversed-phase chromatography on paper have shown that the oxyazocompound quite well extracted into chloroform cobalt, mercury, palladium, gallium, copper, indium, and scandium. Extraction of cobalt, copper, mercury, and palladium is studied in detail with the aid of radioactive indicators (Figure 15).[194]

Cobalt is quantitatively extracted as a chelate CoA_2 (A is the oxyazocompound an-

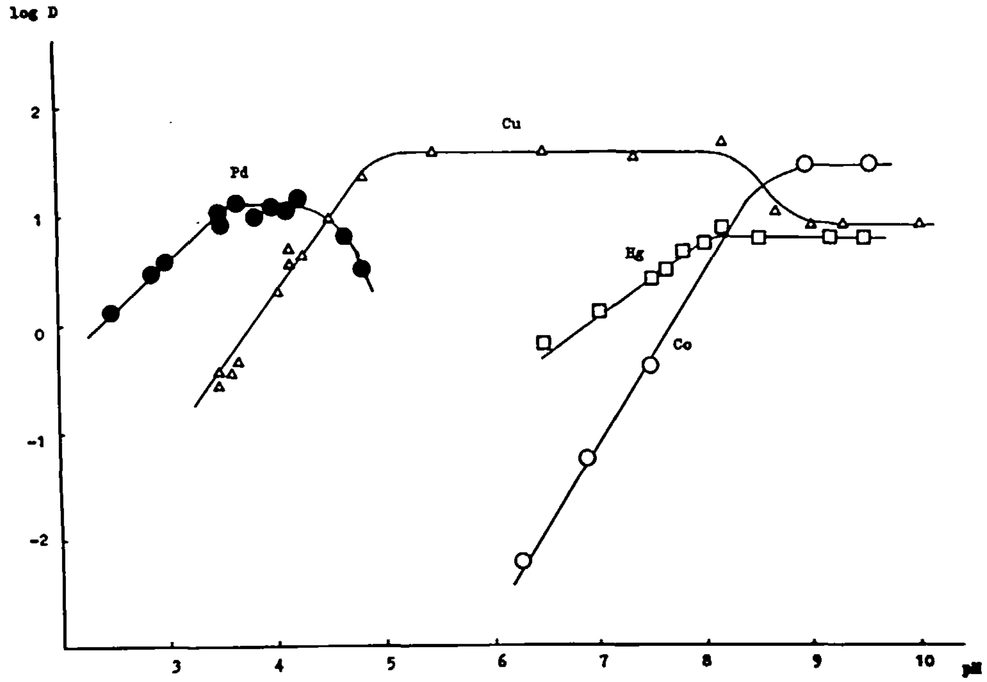


FIGURE 15. Dependence of the distribution ratios of cobalt (O), copper (Δ), mercury (□), and palladium (●) by extraction with oxyazocompound 76 on pH. Concentrations: cobalt, copper, and mercury — 10^{-5} *M*; palladium — 2×10^{-5} *M*; reagent —10^{-3} *M*.

ion) from borate solutions at pH 8.8 to 9.4 in the presence of a 100-fold excess of the reagent. Copper is efficiently extracted from acetate solutions at pH 5 to 8, also, in the presence of a 100-fold excess of oxyazocompound. On the basis of the extraction data the partition and stability constants of the copper chelate CuA_2 being extracted were calculated. Mercury can be quantitatively transferred into the organic phase only after two consecutive extractions in the presence of a 500-fold excess of oxyazocompound and 5% of pyridine by volume. It is assumed that the metal is extracted either in the form of the mixed-ligand complex HgAX or in the form of the ion pair $[HgA]^+X^-$, where X^- is NO_3^- or ClO_4^-.

Recovery of palladium under optimal conditions (pH 3.4 to 4.3, the 100-fold reagent excess) amounts to 94%, though it does not proceed very quickly; in the presence of a 150-fold excess of the spin-labeled oxyazocompound, the phase equilibrium is reached for 40 min; with the 1000-fold reagent excess 15 min are required. Extraction of the metal is probably followed by the formation of the dimer:

$2PdCl_{4\,aq.}^{2-} + 2HA_o \rightleftharpoons [PdACl]_{2\,org.} + 6Cl^- + 2H^+$.

Rather high distribution ratios of the spin-labeled oxyazocompound in the chloroform-water system within the entire pH range and not very high stability of the metal complexes being extracted, which requires a great excess of the reagent for the quantitative extraction of the metal, make it necessary to apply chromatographic separation of the spin-labeled components of the extracts. Using the methods of column liquid absorption chromatography, the chelates of cobalt (cellulose as a sorbent) as well as mercury and palladium (silica gel as a sorbent) were isolated from the extracts. The ESR spectrum of the mercury complex is a quintet; the spectra of cobalt and palladium complexes are presented in Figure 16. The sufficient quantitative elution from the column is achieved only for the palladium complex; it is this system which was used as a basis for the development of the analytical method.

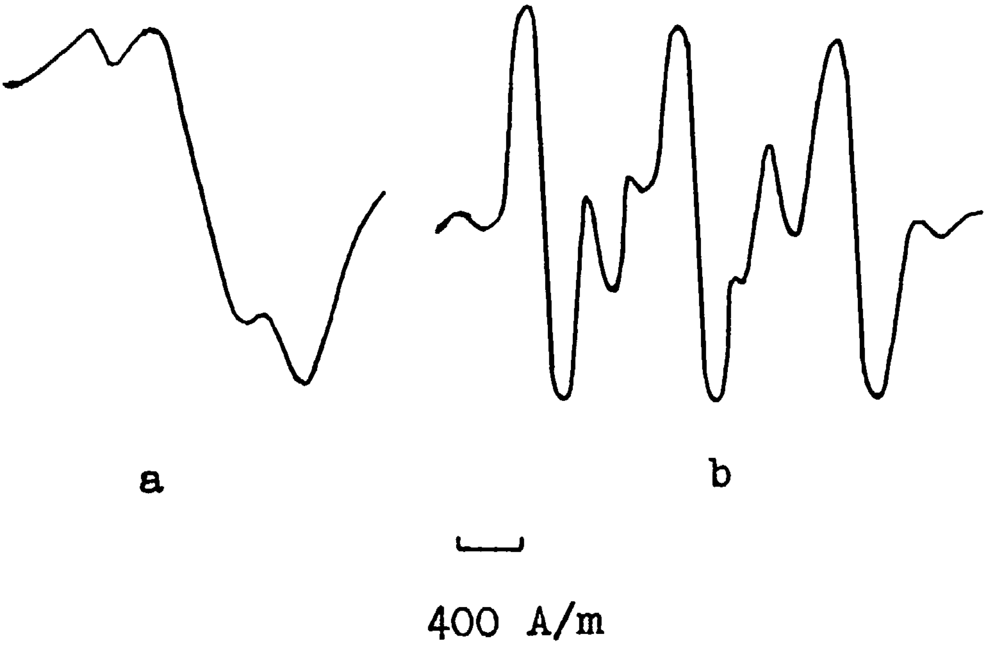


FIGURE 16. ESR spectra of the complexes of cobalt (a) and palladium (b) with oxyazocompound 76 in a chloroform (undeoxygenated) solution (room temperature, X-band, ~10^{-5} *M*, microwave power 5 mW, modulation amplitude 0.8 Oe).

Palladium is extracted into chloroform under the optimal conditions described above. The extract to be separated is transferred to the top of the column with a silica gel (h = 70 mm, d = 10 mm) and the complex, which is more mobile than the reagent, is eluted with a chloroform-ethyl acetate mixture (20:1). A considerable difference in the chromatographic behavior of the chelate and the reagent (on the thin layer chromatograms R_f are equal to 0.59 and 0.15, respectively) makes the separation of these radical-containing components readily available. The amplitude of the ESR spectrum of the eluate fraction containing the spin-labeled palladium chelate is proportional to the palladium concentration in the aqueous phase prior to extraction. With the use of the RE-1306 ESR spectrometer the detection limit was 1×10^{-7} g-ion/*l*. Relative standard deviation of the determination of 1×10^{-6} g-ion/*l* of palladium does not exceed 0.06.

Thus, the work with the spin-labeled oxyazocompound gave one more example of the application of weakly acidic chelating reagent for the determination of the metal with the aid of chromatographic separation.

E. Hydroxyimine [182]

The spin-labeled hydroxyimine 50 exhibits acidic properties in much less degree than oxyazocompound: the value of pK_a exceeds 14. The distribution ratio logarithm value of this compound in the chloroform-water system is also very large: when the aqueous phases are being put to equilibrium with the chloroform solution of hydroxyimine, this spin-labeled reagent remains quantitatively in the organic solvent irrespective of pH of the aqueous solution.

According to the data of the investigations by the method of partition paper chromatography, the reagent is capable of extracting copper, cobalt, zinc, gallium, molybdenum, and vanadium into chloroform. The investigation of the extractive ability of

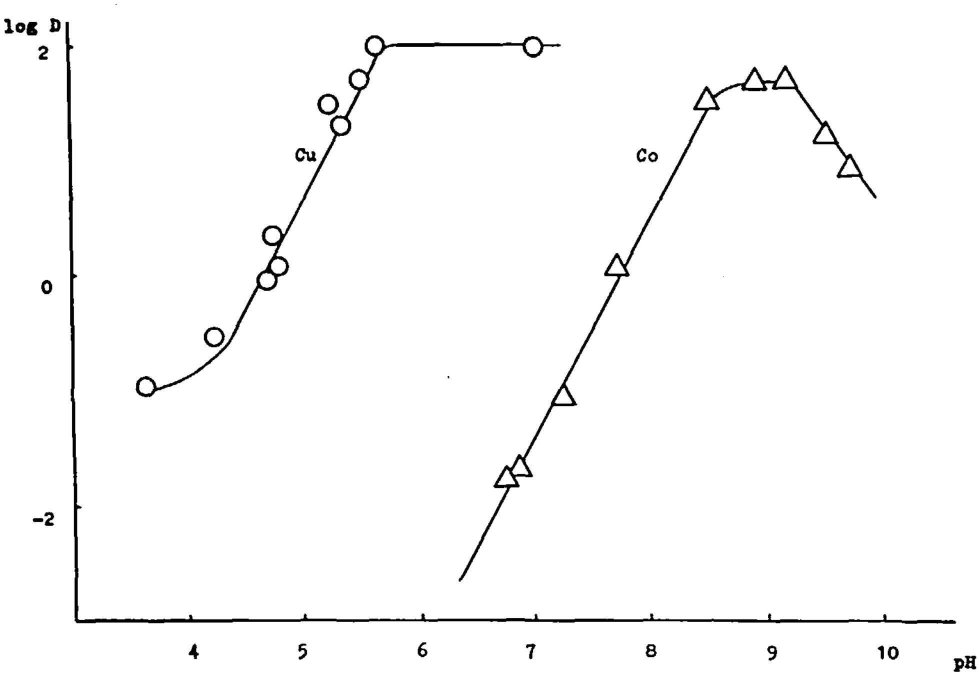


FIGURE 17. Dependence of the distribution ratios of copper and cobalt in the chloroform-water system by extraction with enaminoketone 50 on pH. Concentrations: copper and cobalt — 1×10^{-5} *M;* reagent — 10^{-2} *M*(copper) and 5×10^{-3} *M*(cobalt).

hydroxyimine by the traditional method with the use of radioactive indicators has shown that cobalt is quantitatively extracted at pH 8.3 to 9.4 in the presence of the 500-fold reagent excess (Figure 17). The regularities of extraction correspond to the composition of the compound CoA_2 being extracted (A is the hydroxyimine anion). Copper is recovered by 99% in the chelate of similar composition at pH 5.7 to 8.8 and in the presence of the 1000-fold excess of hydroxyimine (Figure 17). Zinc is quantitatively extracted into chloroform from 0.1 *M* acetate-ammonium buffer solution at pH 8 to 10 in the presence of the 500-fold reagent excess. The extraction constants of these metals were calculated.[182]

Nitroxide-containing hydroxyimine was used for the development of the method of ESR determination of copper.[182] Determination is based on quantitative extraction of the metal into chloroform from the aqueous solution at pH 7 in the presence of no less than a 500-fold excess of the spin-labeled reagent. Separation of the nitroxide-containing copper chelate and the excessive reagent contained in the extract is attained by the method of liquid absorption thin layer chromatography on silica gel with the use of acetone-hexane-chloroform mixture (volume ratio 1:2:10) as a mobile phase. After completing the development of the chromatogram, the sorbent thin layer area possessing nitroxide-containing copper chelate is removed from the plate, transferred to a glass filter, and the chelate is washed out of the silica gel by chloroform. The ESR spectrum of the solution obtained represents a triplet which is not distorted by exchange interaction, despite the presence of the paramagnetic ion in the composition of the complex.[77] Having measured the amplitude of this spectrum, the copper concentration in the aqueous solution prior to extraction is determined from the calibration curve plotted preliminarily. The detection limit with the RE-1306 ESR spectrometer is 5×10^{-7} g-ion/*l*, which is 1.5 to 2 orders of magnitude less than the detection limit of the copper obtained by the ESR method with respect to its own paramagnetism.[30]

Thus, the work with the spin-labeled hydroxyimine exemplifies a possibility to determine paramagnetic metal ion with the nitroxide-containing reagent and demonstrates advantages of such approach in sensitivity.

V. CONCLUSIONS

The reviewed papers on the application of nitroxide-containing reagents for the ESR determination of metals have confirmed the universality of this approach. In fact, with the aid of spin-labeled compounds it is possible to determine both diamagnetic and, at least, some of paramagnetic metal ions, their detection limits being only slightly dependent on the nature of the element determined. Moreover, five compounds of five various classes of chelating reagents were used for analytical purposes, which indicates that the possibility of determining the metals with nitroxide-containing reagents is of universal character and is not confined by specific properties of separate systems.

To a certain extent many other analytical characteristics of the method were studied. The detection limits obtained even with the use of not very sensitive ESR spectrometers and amounting to about 10^{-7} g-ion/*l* were markedly lower than the detection limits of metals obtained with spectrophotometric and many electrochemical methods; they are comparable with the detection limits of the metals obtained by atomic absorption and atomic fluorescence methods. As has already been mentioned, there exist perspectives for lowering the detection limits to 1.5 to 2 orders of magnitude, provided a higher sensitive ESR spectrometer is available. Preliminary degassing of solutions before ESR spectrometric investigation and the application of computer accumulation of spectra were not used in the reviewed works, but surely they will favor the further lowering of the detection limits. The procedures of the determination of metals with nitroxide-containing reagents can also readily include the supplementary operations of extractive and chromatographic concentration.

The method of spin-labeled reagents is quite competitive with the majority of other modern physical methods of analysis with respect to accuracy and precision of the results.

It is difficult at this stage of development to evaluate inambiguously the selectivity of the method. In general, the selectivity of metal determinations with the use of nitroxide-containing reagents is lower than that of direct ESR determinations based on intrinsic paramagnetism of metal ions. The selectivity of the analysis with free-radical reagents is based mainly on the selectivity of the formation and extraction of complexes. It may be predicted that the method of spin-labeled reagents is closed in selectivity to the extraction-spectrophotometric one. It is well known that with the use of effective reagents the extraction-spectrophotometric determinations can be very selective, but the high selectivity is not typical of all the metal ions and the complexing reagents. The first radical-containing reagents investigated cannot be considered as very selective; currently, the study of much more selective reagents is in progress. The understanding of the selectivity possibilities of the method is hampered, also, by the lack of information concerning regularities of the interrelation between the ESR spectrum of the spin-labeled chelate and the nature of the metal ion bound. Therefore, the final evaluation of the selectivity of the method of spin-labeled reagents should be made in the future. Chromatography applied for the separation of the excessive reagent can serve as a means of increasing the determination selectivity. The development of a combination of liquid high-performance chromatographs with ESR spectrometers[249,250] can give perspectives for the further development of the method of radical-containing reagents.

The quickness of the analyses performed by following the method described is determined mainly by the duration of chemical operations, particularly, extraction. In favorable cases (e.g., in determining zinc with xanthate), the analysis lasts 10 to 15 min, though it may also last 1.5 to 2 hr as, for instance, in the case of the mercury-β-diketone system. Such a duration of extraction allows simultaneous performance of parallel analyses; it is also possible to use automatic flow-type extraction systems.

Thus, when highly sensitive ESR spectrometer and spin-labeled analogs of highly selective organic reagents are used, the method described can be competitive with other analytical methods. Its major advantage, in our opinion, is that rather low detection limits depend only slightly on the nature of the metals being determined, a fact characteristic of very few analytical methods. The drawbacks of this method are the necessity of preliminary chemical operations and its inability to perform simultaneous multielement determinations.

The investigations carried out to date are only initial steps in the use of spin labels in analytical chemistry. In the future, the method can be developed in two main directions.

The first direction is to improve the approach already applied and tested. It can include, in particular, synthesis of nitroxide-containing analogs of more selective reagents among the analytical reagents already known, development of the theory relating ESR spectra of the nitroxide-containing chelates to the structure of these compounds, application of modern chromatographic methods (including high performance ones), and application of the techniques developed to specific objects of analysis. Further progress in the direction described will be promoted by comprehensive use of the material accumulated during the long years of work with traditional diamagnetic organic reagents. To make use of the data, it is necessary to take into account the corrections for the effect of the spin-labels upon the analytically important properties of the chelating reagents. The first attempt to elucidate these corrections, i.e., the characteristics of the effects of spin-labeled substituent IX, has already been made.[170,247,365]

The second direction of the development of the method of spin-labeled reagents is to test entirely new varieties of its application. Thus, for example, it can be applied to determine metals in the form of complexes in which the nitroxide group of the ligand is directly coordinated to the metal ion. It follows from the literature[226-232] that as a result of such coordination the nitroxide spectrum is usually greatly changed, which can be of great importance for coping with the problem of interferences from the signal of the reagent excess and for increasing the selectivity of determinations. Spin-labels are also likely to be used along with some procedures of radioanalytical methods. Nitroxide radicals can be used for the indirect determination of the compounds which react with them, yielding diamagnetic products.[363] Thus, an attempt can be made to use the reduction reaction of nitroxides as an indicator in catalytic kinetic methods of analysis. Spin-labeled reagents are likely to successfully replace photometric methods for functional analysis of organic compounds and thus decrease their detection limits substantially.

In a word, the use of stable free radicals along with ESR spectroscopy seems to be a promising direction of research in analytical chemistry.

REFERENCES

1. Wertz, J. E. and Bolton, J. R., *Electron Spin Resonance. Elementary Theory and Practical Applications,* McGraw-Hill, New York, 1972.
2. Guilbault, G. G. and Meisel, T., *Anal. Chem.,* 41, 1100, 1969.
3. Meisel, T. and Guilbault, G. G., *Anal. Chim. Acta,* 50, 143, 1970.

4. Bryson, W. G., Hubbard, D. P., Peake, B. M., and Simpson, J., *Anal. Chim. Acta,* 96, 99, 1978.
5. Solozhenkin, P. M., Sidorenko, G. G., Larin, G. M., and Semenov, E. V., *Dokl. Akad. Nauk S.S.S.R.,* 229, 1138, 1976.
6. Garif'yanov, N. S., Mazitov, R. K., and Usacheva, N. F., *Zh. Anal. Khim.,* 18, 283, 1963.
7. Guilbault, G. G. and Lubrano, G. J., *Anal. Lett.,* 1, 725, 1968.
8. Saraceno, A. J., Fanale, D. T., and Coggeshall, N. D., *Anal. Chem.,* 33, 500, 1961.
9. Marov, I. N., Belyaeva, V. K., Gerlit, Yu. B., Dubrov, Yu. N., Ermakov, A. N., Koblova, A. Z., and Petrova, T. G., *Geokhimiya,* No. 1, 20, 1972.
10. Yamamoto, D. and Ozeki, F., *Bull. Chem. Soc. Jpn.,* 45, 1408, 1972.
11. Solozhenkin, P. M., Vasilenko, L. F., and Loseva, N. P., Analysis and Technology of Noble Metals, Transactions of the 8th Conf. on Chemistry, Analysis and Technology of Noble Metals (in Russian), Novosibirsk, 1969, Metallurgiya, Moscow, 1971, 268.
12. Hanson, G., Szabo, A., and Chasteen, N. D., *Anal. Chem.,* 49, 461, 1977.
13. Solozhenkin, P. M. and Sidorenko, G. G., *Dokl. Akad. Nauk Tadzh. S.S.R.,* 16(5), 45, 1973.
14. Solozhenkin, P. M., Sidorenko, G. G., and Baratova, Z. R., *Dokl. Akad. Nauk Tadzh. S.S.R.,* 17(12), 25, 1974.
15. Borisova, L. V., Plastinina, E. I., Ermakov, A. N., Marov, I. N., and Zhukov, V. V., *Zh. Anal. Khim.,* 33, 1982, 1978.
16. Solozhenkin, P. M., Sidorenko, G. G., Klassen, N. G., and Shvengler, F. A., *Zh. Anal. Khim.,* 30, 2219, 1975.
17. Pittke, E. C., Schoffa, G., and Birkle, M., *Messtechnik,* No. 3, 77, 1973.
18. Kashlinskii, A. I., Konanykhina, L. N., Meister, E. K., and Muratova, G. E., Soviet National Conf. on Present State and Perspectives of Development of Analytical Instrument Engineering up to 1985, Tula, 1975, Section on Instruments for Tests of Air for Toxic and Explosive Gases, Abstracts (in Russian), Moscow, 1975, 139.
19. Knechtel, J. R., Janzen, E. G., and Davis, E. R., *Anal. Chem.,* 50, 202, 1978.
20. Mihelcic, D. and Schindler, R. N., *Ber. Kernforschungsanlage Juelich,* Juel-769-PC, 1971.
21. Foster, H., *Anal. Chem.,* 34, 255R, 1962.
22. Flockhart, B. D. and Pink, R. C., *Talanta,* 12, 529, 1965.
23. Farrar, T. C., *Ann. N.Y. Acad. Sci.,* 137, 323, 1966.
24. Bard, A. J., *Standard Methods of Chemical Analysis,* Vol. 3, 6th ed., Part A, Welcher, F. J., Ed., Van Nostrand, Princeton, 1966, 616.
25. Eargle, D. H., Jr., *Anal. Chem.,* 40, 303R, 1968.
26. Janzen, E. G., *Anal. Chem.,* 44, 113R, 1972.
27. Flockhart, B. D., *Proc. Soc. Anal. Chem.,* 9, 134, 1972.
28. Janzen, E. G., *Anal. Chem.,* 46, 478R, 1974.
29. Wasson, J. R. and Corvan, P. J., *Anal. Chem.,* 50, 92R, 1978.
30. Zolotov, Yu. A., *Euroanalysis III, Reviews on Analytical Chemistry,* Carroll, D. M., Ed., Applied Science Publishers, London, 1979, 13.
31. Wasson, J. R. and Salinas, J. E., *Anal. Chem.,* 52, 50R, 1980.
32. Deiana, S. and Micera, G., *Chim. Ind. (Milan),* 63, 264, 1981.
33. Krishnamurthy, M. V., *Anal. Chim. Acta,* 124, 211, 1981.
34. Waters, W., *The Chemistry of Free Radicals,* Clarendon Press, Oxford, 1946.
35. Forrester, A. R., Hay, J. M., and Thompson, R. H., *Organic Chemistry of Stable Free Radicals,* Academic Press, London, 1968.
36. Hamilton, C. L. and McConnell, H. M., *Structural Chemistry and Molecular Biology,* Rich, A. and Davidson, N., Eds., W. H. Freeman, San Francisco, 1968, 115.
37. Radionov, V. A. and Rozantsev, E. G., *Long-lived Radicals* (in Russian), Nauka, Moscow, 1972.
38. Buchachenko, A. L. and Vasserman, A. M., *Stable Radicals, Electron Structure, Reactivity and Application,* Khimia, Moscow, 1973.
39. Kochi, J. K., Ed., *Free Radicals,* John Wiley & Sons, New York, 1973.
40. Forrester, A. R., *Int. Rev. Sci.: Org. Chem.,* Ser. 2, Vol. 10, Waters, W. A., Ed., Butterworths, London, 1975, 87.
41. Nonhebel, D. C. and Walton, J. C., *Free-Radical Chemistry, Structure and Mechanism,* University Press, Cambridge, 1974.
42. Rozantsev, E. G. and Sholle, V. D., *Organic Chemistry of Free Radicals* (in Russian), Khimiya, Moscow, 1979.
43. Berliner, L. J., Ed., *Spin Labelling, Theory and Applications,* Academic Press, New York, 1976.
44. Rozantsev, E. G., *Free Nitroxide Radicals,* Plenum Press, New York, 1970.
45. Rozantsev, E. G. and Sholle, V. D., *Usp. Khimii,* 40, 417, 1971.
46. Zhdanov, R. I., *Nitroxyl Radicals in Chemistry and Biology* (in Russian), Znanie, Moscow, 1973.
47. Keana, J. F. W., *Chem. Rev.,* 78, 37, 1978.

48. Volodarskii, L. B., Grigor'ev, I. A., and Sagdeev, R. Z., *Biological Magnetic Resonance*, Vol. 2, Berliner, L. J. and Reuben, J., Eds., Plenum Press, New York, 1980, 169.
49. Grigor'ev, I. A., Shchukin, G. I., and Volodarskii, L. B., *Izv. Sib. Otd. Akad. Nauk S.S.S.R. Ser. Khim. Nauk,* No. 9/4, 135, 1977.
50. Skripnichenko, L. N., Shapiro, A. B., Rozantsev, E. G., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 109, 1982.
51. Skripnichenko, L. N., Shapiro, A. B., Sholle, V. D., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 681, 1980.
52. Shapiro, A. B., Skripnichenko, L. N., Pavlikov, V. V., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 151, 1979.
53. Zolotov, Yu. A., Petrukhin, O. M., Kurdyukova, N. A., Zhukov, V. V., and Marov, I. N., *Zh. Anal. Khim.,* 33, 1307, 1978.
54. Briere, R., Giroud, A. M., Rassat, A., and Rey, P., *Bull. Soc. Chim. Fr.,* No. 3/4, Part 2, 147, 1980.
55. Briere, R., Espie, J. C., Ramasseul, R., Rassat, A., and Rey, P., *Tetrahedron Lett.,* No. 11, 941, 1979.
56. Wong, L. T. L., Schwenk, R., and Hsia, J. C., *Can. J. Chem.,* 52, 3381, 1974.
57. Rozantsev, E. G. and Krinitskaya, L. A., *Tetrahedron,* 21, 491, 1965.
58. Kosman, D. and Piette, L. H., *Chem. Commun.,* No. 16, 926, 1969.
59. Fedrigolli, R. and Schwarzhans, K. E., *Z. Naturforsch. B,* 35B, 68, 1980.
60. Golubev, V. A., Neiman, M. B., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 343, 1966.
61. Volodarskii, L. B., Grigor'ev, I. A., and Kutikova, G. A., *Zh. Org. Khim.,* 9, 1974, 1973.
62. Kosman, D. J., Hsia, J. C., and Piette, L. H., *Arch. Biochem. Biophys.,* 133, 29, 1969.
63. Williams, J. C., Mehlhorn, R., and Keith, A. D., *Chem. Phys. Lipids,* 7, 207, 1971.
64. Manafova, R. A., Mamedov, I. M., Medzhidov, A. A., Mamed'yarov, G. M., and Shakhtakhtinskii, T. N., *Zh. Obshch. Khim.,* 50, 1362, 1980.
65. Golubev, V. A. and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 716, 1965.
66. Keana, J. F. W. and LaFleur, L. E., *Chem. Phys. Lipids,* 23, 253, 1979.
67. Lee, T. D., Birrell, G. B., and Keana, J. F. W., *J. Am. Chem. Soc.,* 100, 1618, 1978.
68. Jost, P., Libertini, L. J., Hebert, V. C., and Griffith, O. H., *J. Mol. Biol.,* 59, 77, 1971.
69. Kedik, S. A., Rozantsev, E. G., and Usvyatsov, A. A., *Dokl. Akad. Nauk S.S.S.R.,* 257, 1382, 1981.
70. Rozantsev, E. G., Dagonneau, M., Kagan, E. S., Mikhailov, V. I., and Scholle, V. D., *J. Chem. Res. Synop.,* No. 8, 260, 1979.
71. Roberts, G. C. K., Hannah, J., and Jardetzky, O., *Science,* 165, 504, 1969.
72. Ullman, E. F. and Schneider, R. S., U.S. Patent 3,716,335, 1973.
73. Otaga, R. T., McConnell, H. M., and Jones, R. T., *Biochem. Biophys. Res. Commun.,* 47, 157, 1972.
74. Shchukin, G. I. and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 228, 1979.
75. Ishizu, K., Kohama, H., and Mukai, K., *Chem. Lett.,* p. 227, 1978.
76. Grigor'ev, I. A. and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 208, 1978.
77. Larionov, S. V., Ovcharenko, V. I., Kirichenko, V. N., Mokhosoeva, V. K., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 14, 1982.
78. Rassat, A. and Rey, P., *Bull. Soc. Chim. Fr.,* p. 815, 1967.
79. Hankovszky, H. O., Hideg, K., Lex, L., and Tigyi, J., *Synthesis,* p. 530, 1979.
80. Volodarskii, L. B., Kutikova, G. A., Kobrin, V. S., Sagdeev, R. Z., and Molin, Yu. N., *Izv. Sib. Otd. Akad. Nauk S.S.S.R. Ser. Khim. Nauk,* No. 7/3, 101, 1971.
81. Schneider, R. S. and Ullman, E. F., U.S. Patent 3,749,644, 1973.
82. Rzaev, A. A., Medzhidov, A. A., and Mamedov, Kh. S., *Zh. Neorg. Khim.,* 25, 1277, 1980.
83. Martin, V. V. and Volodarskii, L. B., U.S.S.R. Author's Certificate No. 697509, 1979.
84. Medzhidov, A. A., Kirichenko, L. N., and Likhtenshtein, G. I., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 698, 1969.
85. Mamedova, Yu. G., Babaeva, L. I., and Rozantsev, E. G., *Koord. Khim.,* 6, 491, 1980.
86. Medzhidov, A. A., Shapiro, A. B., Mamedova, P. Sh., Musaev, A. M., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 538, 1977.
87. Mamedova, Yu. G., Medzhidov, A. A., and Kolomina, L. N., *Zh. Neorg. Khim.,* 17, 2946, 1972.
88. Medzhidov, A. A., Kutovaya, T. M., Rodin, N. P., Guseinova, M. K., Timakov, I. A., and Mamedov, Kh. S., *Koord. Khim.,* 5, 1433, 1979.
89. Kelareva, M. P., Zolotov, Yu. A., Bodnya, V. A., Volodarskii, L. B., and Reznikov, V. A., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.,* p. 1434, 1981.
90. Helbert, J. N., Kopf, P. W., Poindexter, E. H., and Wagner, B. E., *J. Chem. Soc. Dalton Trans.,* p. 998, 1975.
91. Ullman, E. F. and Boocock, D. G. B., *Chem. Commun.,* p. 1161, 1969.

92. Grigor'ev, I. A., Druganov, A. G., and Volodarskii, L. B., *Izv. Sib. Otd. Akad. Nauk S.S.S.R. Ser. Khim. Nauk.*, No. 9/4, 131, 1976.
93. Wagner, B. E., Helbert, J. N., Bates, R. D., and Poindexter, E. H., *Chem. Commun.*, p. 748, 1973.
94. Jahr, D., Rebhan, K. H., Schwarzhans, K. E., and Wiedemann, J., *Z. Naturforsch. B*, 28B, 55, 1973.
95. Shapiro, A. B., Novozhilova, G. A., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 452, 1976.
96. Jahr, D., Schwarzhans, K. E., Nöthe, D., and Burkert, P. K., *Z. Naturforsch. B*, 26B, 1210, 1971.
97. Grigor'ev, I. A., Shchukin, G. I., Druganov, A. G., and Volodarskii, L. B., *Izv. Sib. Otd. Akad. Nauk S.S.S.R. Ser. Khim. Nauk*, No. 2/1, 80, 1979.
98. Kirichenko, L. N. and Medzhidov, A. A., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 2849, 1969.
99. Larionov, S. V., Ovcharenko, V. I., and Sagdeev, R. Z., *Koord. Khim.*, 5, 1034, 1979.
100. Sevast'yanova, T. K. and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 2339, 1972.
101. Parmon, V. N., Kokorin, A. I., and Zhidomirov, G. M., *Stable Biradicals* (in Russian), Nauka, Moscow, 1980.
102. Volodarskii, L. B., *Khim. Geterotsikl. Soedin.*, p. 1299, 1973.
103. Rozantsev, E. G., *Usp. Khim.*, 35, 1549, 1966.
104. Volodarskii, L. B., Kutikova, G. A., Sagdeev, R. Z., and Molin, Yu. N., *Tetrahedron Lett.*, p. 1065, 1968.
105. Osiecki, J. H. and Ullman, E. F., *J. Am. Chem. Soc.*, 90 , 1078, 1968.
106. Keana, J. F. W., Lee, T. D., and Bernard, E. M., *J. Am. Chem. Soc.*, 98, 3052, 1976.
107. Lebedev, O. L. and Kazarnovskii, S. N., *Trudy Po Khimii I Khimicheskoi Tekhnologii (Gorki)*, No. 3, 649, 1959.
108. Golding, B. T., Ioannou, P. V., and O'Brien, M. M., *Synthesis*, p. 462, 1975.
109. Caproiu, M. T., Negoita, N., and Balaban, A. T., *Tetrahedron Lett.*, p. 1825, 1977.
110. Berthier, G., Lemaire, H., Rassat, A., and Veillard, A., *Theor. Chim. Acta*, 3, 213, 1965.
111. Douady, J., Ellinger, Y., Rassat, A., Subra, R., and Berthier, G., *Mol. Phys.*, 17, 217, 1969.
112. Kikuchi, O., *Bull. Chem. Soc. Jpn.*, 42, 1187, 1969.
113. Morokuma, K., *J. Am. Chem. Soc.*, 91, 5412, 1969.
114. Abronin, I. A., Sysoeva, N. A., Zhidomirov, G. M., Buchachenko, A. L., and Chuvylkin, N. D., *Zh. Strukt. Khim.*, 12, 985, 1971.
115. Rozantsev, E. G. and Gur'yanova, E. N., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 979, 1966.
116. Ayscough, P. B. and Sargent, F. P., *J. Chem. Soc.*, B, p. 907, 1966.
117. Kikuchi, O. and Someno, K., *Bull. Chem. Soc. Jpn.*, 40, 2549, 1967.
118. Briere, R., Lemaire, H., and Rassat, A., *J. Chem. Phys.*, 48, 1429, 1968.
119. Briere, R., Chapelet-Letourneux, G., Lemaire, H., and Rassat, A., *Mol. Phys.*, 20, 211, 1971.
120. Ferrieu, F. and Nechtschein, M., *Chem. Phys. Lett.*, 11, 46, 1971.
121. Mahoney, L. R., Mendenhall, G. D., and Ingold, K. U., *J. Am. Chem. Soc.*, 95, 8610, 1973.
122. Ullman, E. F., Call, L., and Osiecki, J. H., *J. Org. Chem.*, 35, 3623, 1970.
123. Ellinger, Y., Subra, R., Rassat, A., Douady, J., and Berthier, G., *J. Am. Chem. Soc.*, 97, 476, 1975.
124. Davis, T. D., Christoffersen, R. E., and Maggiora, G. M., *J. Am. Chem. Soc.*, 97, 1347, 1975.
125. Janzen, E. G., *Topics in Stereochemistry*, Vol. 6, Allinger, N. L. and Eliel, E. L., Eds., John Wiley & Sons, New York, 1971, 177.
126. Shibaeva, R. P., *Zh. Strukt. Khim.*, 16, 330, 1975.
127. Hoffman, A. K. and Henderson, A. T., *J. Am. Chem. Soc.*, 83, 4671, 1961.
128. Linnett, J. W., *J. Am. Chem. Soc.*, 83, 2643, 1961.
129. Bowman, D. F., Gillan, T., and Ingold K. U., *J. Am. Chem. Soc.*, 93, 6555, 1971.
130. Martinie-Hombrouck, J. and Rassat, A., *Tetrahedron*, 30, 433, 1974.
131. Briere, R. and Rassat, A., *Tetrahedron*, 32, 2891, 1976.
132. Keana, J. F. W., Dinerstein, R. J., and Baitis, F., *J. Org. Chem.*, 36, 209, 1971.
133. Kasaikina, O. T., Lobanova, T. B., Rozynov, B. V., and Emanuel, N. M., *Dokl. Akad. Nauk S.S.S.R.*, 249, 647, 1979.
134. Golubev, V. A., Rozantsev, E. G., and Neiman, M. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 1927, 1965.
135. Abakumov, G. A. and Tikhonov, V. D., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 796, 1969.
136. Hoffman, B. M. and Eames, T. B., *J. Am. Chem. Soc.*, 91, 2169, 1969.
137. Golubev, V. A. and Sen, V. D., U.S.S.R. Natl. Conf. on Nitroxide Radicals (in Russian), Abstracts, May 12 to 14, 1982, Chernogolovka, 1982, 8.
138. Solomatin, V. T. and Ozhegov, P. I., *Zh. Anal. Khim.*, 28, 2129, 1973.
139. Golubev, V. A., Sen, V. D., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 2773, 1974.

140. Zhdanov, R. I., Romashina, T. N., Volodarskii, L. B., and Rozantsev, E. G., *Dokl. Akad. Nauk S.S.S.R.*, 236, 605, 1977.
141. Neiman, M. B., Mairanovskii, S. G., Kovarskaya, B. M., Rozantsev, E. G., and Gintsberg, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 1518, 1964.
142. Sudnik, M. V. and Romantsev, M. F., *Zh. Obshch. Khim.*, 42, 743, 1972.
143. Serve, D., *Electrochim. Acta*, 20, 469, 1975.
144. Tsunaga, M., Iwakura, C., and Tamura, H., *Electrochim. Acta*, 18, 241, 1973.
145. Sümmermann, W. and Deffner, U., *Tetrahedron*, 31, 593, 1975.
146. Solomatin, V. T. and Kharlamova, L. I., *Zh. Anal. Khim.*, 29, 1497, 1974.
147. Pokhodenko, V. D., Beloded, A. A., and Koshechko, V. G., *Redox Reactions of Free Radicals* (in Russian), Naukova Dumka, Kiev, 1977.
148. Golubev, V. A., Sholle, V. D., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 1204, 1972.
149. Zhdanov, R. I., Golubev, V. A., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 186, 1970.
150. Golubev, V. A., Voronina, G. N., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 161, 1972.
151. Takaya, Y., Matsubayashi, G., and Tanaka, T., *Inorg. Chim. Acta*, 6, 339, 1972.
152. Golubev, V. A., Zhdanov, R. I., Gida, V. M., and Rozantsev, E. G., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 2815, 1970.
153. Khudyakov, I. V. and Kuz'min, V. A., *Usp. Khim.*, 47, 39, 1978.
154. Davydov, R. M., *Zh. Fiz. Khim.*, 42, 2639, 1968.
155. Lee, T. D. and Keana, F. W., *J. Org. Chem.*, 40, 3145, 1975.
156. Sosnovsky, G. and Konieczny, M., *Synthesis*, p. 619, 1977.
157. Dikanov, S. A., Grigor'ev, I. A., Volodarskii, L. B., and Tsvetkov, Yu. D., U.S.S.R. Natl. Conf. on Nitroxide Radicals, Abstracts, May 12 to 14, 1982, Chernogolovka, 1982, 53.
158. Golubev, V. A., Sen, V. D., Kulyk, I. V., and Aleksandrov, A. A., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 2235, 1975.
159. Morozova, I. D. and Dyatkina, M. E., *Usp. Khim.*, 37, 865, 1968.
160. Hudson, A., *Electron Spin Resonance*, Vol. 8, Ayscough, P. B., Ed., The Chemical Society, London, 1984, 46.
161. Baldin, V. I., Izyumova, T. G., and Putyrskii, V. P., *Zh. Strukt. Khim.*, 20, 289, 1979.
162. Mukhtarov, A. Sh., Il'yasov, A. V., Levin, Ya. A., Gozman, I. P., Skorobogatova, M. S., and Zoroatskaya, E. I., *Teor. Eksp. Khim.*, 12, 831, 1976.
163. Stout, G. and Engberts, J. B. F. N., *J. Org. Chem.*, 39, 3800, 1974.
164. Sullivan, P. D. and Menger, E. M., *Adv. Magn. Reson.*, 9, 1, 1977.
165. Kuznetsov, A. N. and Kuznetsov, V. A., *Zh. Strukt. Khim.*, 18, 967, 1977.
166. Likhtenshtein, G. I., Grebenshchikov, Yu. B., and Medzhidov, A. A., *Zh. Fiz. Khim.*, 44, 812, 1970.
167. Evstiferov, M. V., Vanifatova, N. G., Petrukhin, O. M., Zolotov, Yu. A., and Volodarskii, L. B., U.S.S.R. Natl. Conf. on Nitroxide Radicals, Abstracts, May 12 to 14, 1982, Chernogolovka, 1982, 61.
168. Makarshin, L. L. and Berdnikov, V. M., *Teor. Eksp. Khim.*, 16, 195, 1980.
169. Yager, T. D., Eaton, G. R., and Eaton, S. S., *Chem. Commun.*, p. 944, 1978.
170. Zolotov, Yu. A., Petrukhin, O. M., Nagy, V. Yu., and Volodarskii, L. B., *Anal. Chim. Acta*, 115, 1, 1980.
171. Petrukhin, O. M., Nagy, V. Yu., and Zolotov, Yu. A., in EUCHEM Conf. on Stable Free Nitroxide Radicals, Synthesis and Applications, Hämeenlinna, Finland, August 20 to 22, 1981, The Finland Chemical Society, Helsinki, 1981, 29.
172. Petrukhin, O. M., Nagy, V. Yu., and Volodarskii, L. B., *Koord. Khim.*, 9, 298, 1983.
173. Briere, R., Rassat, A., and Rey, P., *J. Am. Chem. Soc.*, 100, 343, 1978.
174. Veyret, C. and Blaise, A., *Mol. Phys.*, 25, 873, 1973.
175. Espie, J. C., Laugier, J., Ramasseul, R., Rassat, A., and Rey, P., *Nouv. J. Chim.*, 4, 205, 1980.
176. Weissgerber, R. and Schwarzhans, K. E., *Z. Naturforsch.*, 31B, 208, 1976.
177. Medzhidov, A. A., Timakov, I. A., and Mamedova, Yu. G., *Zh. Strukt. Khim.*, 18, 714, 1977.
178. Dalal, D. P., Eaton, S. S., and Eaton, G. R., *J. Magn. Reson.*, 42, 277, 1981.
179. Krinitskaya, L. A. and Dobryakov, S. N., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 582, 1966.
180. Larionov, S. V., Ovcharenko, V. I., Kirichenko, V. N., Sagdeev, R. Z., and Volodarskii, L. B., *Koord. Khim.*, 4, 1878, 1978.
181. Larionov, S. V., Mironova, G. N., Ovcharenko, V. I., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 977, 1980.
182. Kelareva, M. P., Gromova, T. A., Bodnya, V. A., Volodarskii, L. B., Reznikov, V. A., and Zolotov, Yu. A., *Zh. Anal. Khim.*, 37, 1563, 1982.

183. Kozhemyak, N. V., Podberezskaya, N. V., and Bakakin, V. V., *Zh. Strukt. Khim.*, 21(5), 124, 1980.
184. Larionov, S. V., Ovcharenko, V. I., Sadykov, R. A., Sagdeev, R. Z., and Volodarskii, L. B., *Koord. Khim.*, 1, 1312, 1975.
185. Sadykov, R. A., Sagdeev, R. Z., Molin, Yu. N., Ovcharenko, V. I., Larionov, S. V., and Volodarskii, L. B., *Koord. Khim.*, 3, 71, 1977.
186. Dorfer, A. and Schwarzhans, K. E., *Z. Naturforsch.*, 38B, 265, 1983.
187. Eaton, S. S. and Eaton, G. R., *Inorg. Nucl. Chem. Lett.*, 15, 29, 1979.
188. Stryukov, V. B., Fedutin, D. N., and Zvarykina, A. V., *Pis'ma Zh. Eksper. Teor. Fiz.*, 19, 687, 1974.
189. Eaton, G. R., *Inorg. Nucl. Chem. Lett.*, 8, 647, 1972.
190. Guseinova, M. K. and Mamedov, S. D., *Zh. Strukt. Khim.*, 19, 702, 1978.
191. Atovmyan, L. O., Golovina, N. I., Klitskaya, G. A., Medzhidov, A. A., Zvarykina, A. V., Stryukov, V. B., and Fedutin, D. N., *Zh. Strukt. Khim.*, 16, 624, 1975.
192. Rodin, N. P., Medzhidov, A. A., Kutovaya, T. M., and Guseinova, M. K., *Zh. Strukt. Khim.*, 22, 85, 1981.
193. Shnulin, A. N., Struchkov, Yu. T., Mamedov, Kh. S., Medzhidov, A. A., and Kutovaya, T. M., *Zh. Strukt. Khim.*, 18, 1006, 1977.
194. Zolotov, Yu. A., Bodnya, V. A., Kelareva, M. P., Morosanova, E. I., Volodarskii, L. B., and Reznikov, V. A., *Zh. Anal. Khim.*, 37, 981, 1982.
195. Ovcharenko, V. I., Larionov, S. V., Sadykov, R. A., Sagdeev, R. Z., Grigor'ev, I. A., and Volodarskii, L. B., *Koord. Khim.*, 3, 1558, 1977.
196. Ovcharenko, V. I., Larionov, S. V., Sagdeev, R. Z., and Volodarskii, L. B., *Izv. Sib. Otd. Akad. Nauk S.S.S.R. Ser. Khim. Nauk*, No. 7/3, 79, 1978.
197. Ovcharenko, V. I., Larionov, S. V., Sagdeev, R. Z., and Volodarskii, L. B., *Zh. Strukt. Khim.*, 19, 163, 1978.
198. Ovcharenko, V. I. and Larionov, S. V., *Zh. Neorg. Khim.*, 26, 2758, 1981.
199. Solozhenkin, P. M., Shvengler, F. A., and Rakitina, E. V., *Dokl. Akad. Nauk Tadzh. S.S.R.*, 20(4), 25, 1977.
200. Solozhenkin, P. M., Klassen, N. G., and Shvengler, F. A., *Zh. Anal. Khim.*, 32, 2080, 1977.
201. Solozhenkin, P. M., Klassen, N. G., Rakitina, E. V., and Spiridonova, G. L., *Dokl. Akad. Nauk Tadzh. S.S.R.*, 21(4), 28, 1978.
202. Shvengler, F. A., Solozhenkin, P. M., and Rakitina, E. V., *Dokl. Akad. Nauk Tadzh. S.S.R.*, 17(9), 40, 1974.
203. Ovcharenko, V. I., Larionov, S. V., Mironova, G. N., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 645, 1979.
204. Shapiro, A. B., Volodarskii, L. B., Krasochka, O. N., and Atovmyan, L. O., *Dokl. Akad. Nauk S.S.S.R.*, 254, 1140, 1980.
205. Shapiro, A. B., Volodarskii, L. B., Krasochka, O. N., and Atovmyan, L. O., *Dokl. Akad. Nauk S.S.S.R.*, 255, 1146, 1980.
206. DuBois, D. L., Eaton, G. R., and Eaton, S. S., *J. Am. Chem. Soc.*, 100, 2686, 1978.
207. Braden, G. A., Trevor, K. T., Neri, J. M., Greenslade, D. J., Eaton, G. R., and Eaton, S. S., *J. Am. Chem. Soc.*, 99, 4854, 1977.
208. Eaton, S. S., DuBois, D. L., and Eaton, G. R., *J. Magn. Reson.*, 32, 251, 1978.
209. DuBois, D. L., Eaton, G. R., and Eaton, S. S., *J. Am. Chem. Soc.*, 101, 2624, 1979.
210. DuBois, D. L., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 18, 75, 1979.
211. More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 18, 2492, 1979.
212. Eaton, S. S., More, K. M., DuBois, D. L., Boymel, P. M., and Eaton, G. R., *J. Magn. Reson.*, 41, 150, 1980.
213. Eaton, S. S., DuBois, D. L., Boymel, P. M., and Eaton, G. R., *J. Phys. Chem.*, 83, 3323, 1979.
214. More, K. M., Eaton, S. S., and Eaton, G. R., *Inorg. Chem.*, 20, 2641, 1981.
215. Sawant, B. M., Braden, G. A., Smith, R. E., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 20, 3349, 1981.
216. More, K. M., Sawant, B. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 20, 3354, 1981.
217. Hata, S. and Tsuchida, E., *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, 20, 514, 1979.
218. Beck, W., Schorp, K., and Stetter, K. H., *Z. Naturforsch.*, 26B, 684, 1971.
219. Ovcharenko, V. I., Synthesis and Physico-Chemical Investigation of Metal Complexes with Some Derivatives of Stable Nitroxyl Radicals of Imidazoline and Imidazolidine, thesis of the dissertation of Candidate of Chemical Sciences, Novosibirsk, 1979.
220. Sadykov, R. A., Investigation of Some Complexes of Transition Metals with Stable Nitroxyl Radicals by Methods of Magnetic Resonance, thesis of the dissertation of Candidate of Chemical Sciences, Novosibirsk, 1976.
221. Eaton, S. S. and Eaton, G. R., *Coord. Chem. Rev.*, 26, 207, 1978.

222. Larionov, S. V., *Zh. Strukt. Khim.*, 23, 125, 1982.
223. Lim, Y. Y. and Drago, R. S., *Inorg. Chem.*, 11, 1334, 1972.
224. Salikhov, K. M., Doctorov, A. B., Molin, Yu. N., and Zamaraev, K. I., *J. Magn. Reson.*, 5, 189, 1971.
225. Mamedova, Yu. G. and Rozantsev, E. G., *Koord. Khim.*, 6, 739, 1980.
226. Zelonka, R. A. and Baird, M. C., *J. Am. Chem. Soc.*, 93, 6066, 1971.
227. Karayannis, N. M., Paleos, C. M., Mikulski, C. M., Pytlewski, L. L., Blum, H., and Labes, M. M., *Inorg. Chim. Acta*, 7, 74, 1973.
228. Cohen, A. H. and Hoffman, B. M., *J. Am. Chem. Soc.*, 95, 2061, 1973.
229. Mikulski, C. M., Gelfand, L. S., Pytlewski, L. L., Skryantz, J. S., and Karayannis, N. M., *Transit. Metal. Chem.*, 3, 276, 1978.
230. Eames, T. B. and Hoffman, B. M., *J. Am. Chem. Soc.*, 93, 3141, 1971.
231. Abakumov, G. A. and Tikhonov, V. D., *Zh. Strukt. Khim.*, 13, 150, 1972.
232. Abakumov, G. A., Tikhonov, V. D., and Razuvaev, G. A., *Dokl. Akad. Nauk S.S.S.R.*, 187, 571, 1969.
233. Zolotov, Yu. A., *Extraction of Chelate Compounds*, Ann Arbor-Humphrey Scientific Publishers, Ann Arbor, 1970.
234. Stary, J., *The Solvent Extraction of Metal Chelates*, Pergamon Press, Oxford, 1964.
235. Shamaev, V. I., *J. Radioanal. Chem.*, 57, 337, 1980.
236. Goldberg, I. B., *J. Magn. Reson.*, 32, 233, 1978.
237. Eaton, S. S. and Eaton, G. R., *Bull. Magn. Reson.*, 1, 130, 1980.
238. Goldberg, I. B. and Crowe, H. R., *Anal. Chem.*, 49, 1353, 1977.
239. Solozhenkin, P. M. and Sidorenko, G. G., ESR Control of the Content of Metals in Ore Pulps and Solutions, TsNIITEITsvetmet, Moscow, 1973, 42.
240. Solozhenkin, P. M., Zinchenko, Z. A., and Sidorenko, G. G., *Control of the Ionic Composition of Ore Pulp upon Flotation*, Suvorovskaya, N. A. and Okolovich, A. M., Eds., Nauka, Moscow, 1974, 145.
241. Solozhenkin, P. M., Klassen, N. G., and Sidorenko, G. G., U.S.S.R. Author's Certificate No. 448,023, 1974.
242. Nagy, V. Yu., Evstiferov, M. V., Petrukhin, O. M., Volodarskii, L. B., and Zolotov, Yu. A., *Anal. Chim. Acta*, 128, 85, 1981.
243. Larionov, S. V., Ovcharenko, V. I., Sadykov, R. A., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 1922, 1975.
244. Nagy, V. Yu., Petrukhin, O. M., Zolotov, Yu. A., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 2186, 1978.
245. Nagy, V. Yu., Development of the Method of Analysis Based on Extraction of Metal Complexes with Radical-Containing Complexing Reagents, author's abstract of the thesis of the dissertation of Candidate of Chemical Sciences, Moscow, 1981.
246. Grigor'ev, I. A., Shchukin, G. I., and Volodarskii, L. B., U.S.S.R. Natl. Conf. on Nitroxide Radicals, Abstracts, May 12 to 14, 1982, Chernogolovka, 1982, 9.
247. Nagy, V. Yu., Development of the Method of Analysis Based on Extraction of Metal Complexes with Radical-Containing Complexing Reagents, thesis of the dissertation of Candidate of Chemical Sciences, Moscow, 1980.
248. Irving, H. M. N. H., *Ion Exchange and Solvent Extraction*, Vol. 6, Marinsky, J. A. and Marcus, Y., Eds., Marcel Dekker, New York, 1974, 139.
249. Rokushika, S., Taniguchi, H., and Hatano, H., *Anal. Lett.*, 8, 205, 1975.
250. Makino, K., Suzuki, N., Moriya, F., Rokushika, S., and Hatano, H., *Chem. Lett.*, p. 675, 1979.
251. Sakane, Y., Saito, K., Matsumoto, K., and Osajima, Y., *Bunseki Kagaku*, 30, 715, 1981.
252. Bryson, W. G., Hubbard, D. P., Peake, B. M., and Simpson, J., *Anal. Chim. Acta*, 116, 353, 1980.
253. Zherebin, Yu. L., Kovtun, V. D., and Bogatskii, A. V., *Zh. Anal. Khim.*, 36, 1850, 1981.
254. Ichiki, M., Isobe, T., and Tarutani, T., *Mem. Fac. Sci. Kyushu Univ. Ser. C*, 11, 41, 1978.
255. Carpenter, R., *Geochim. Cosmochim. Acta*, 47, 875, 1983.
256. Klassen, N. G., Sidorenko, G. G., and Solozhenkin, P. M., *Izv. AN Tadzh. S.S.R. Otd. Fiz.-Mat. Geol.-Khim. Nauk*, 1, 95, 1979.
257. Solozhenkin, P. M., Sidorenko, G. G., Larin, G. M., Shalukhina, L. M., and Glukhov, I. A., *Zh. Anal. Khim.*, 34, 808, 1979.
258. Sanke Govda, Kh., Solozhenkin, P. M., Semenov, E. V., and Radkharani, B. G., *Dokl. AN Tadzh. S.S.R.*, 23(1), 21, 1980.
259. Watanabe, T., *Bunseki*, p. 807, 1981.
260. Goldberg, I. B., *Electron Spin Reson.*, 6, 1, 1981.
261. Wasson, J. R., *Anal. Chem.*, 54, 121R, 1982.

262. Wasson, J. R., *Anal. Chem.*, 56, 129R, 1984.
263. Goldberg, I. B. and Bard, A. J., *Treatise on Analytical Chemistry*, Vol. 6, 2nd ed., Part 1, Kolthoff, I. M., Elving, P. J., and Bursey, M. M., Eds., Wiley-Interscience, New York, in press.
264. Brinkman, W. J. and Freiser, H., *Anal. Lett.*, 4, 513, 1971.
265. Abakumov, G. A., Cherkasov, V. K., and Lobanov, A. V., Organic Reagents in Analytical Chemistry, abstracts of papers of the 5th U.S.S.R. Natl. Conf. (in Russian), Part 2, Kiev, 1983, Naukova Dumka, Kiev, 1983, 120.
266. Stegmann, H. B., Nagel, E., Merkle, R., and Scheffer, K., *Fresenius' Z. Anal. Chem.*, 316, 678, 1983.
267. Reznikov, V. A., Reznikova, T. I., and Volodarskii, L. B., *Zh. Org. Khim.*, 18, 2135, 1982.
268. Patrina, L. A., Ovcharenko, V. I., and Larionov, S. V., *Zh. Neorg. Khim.*, 29, 1605, 1984.
269. Singh, H. B., Osthana, S., and Maheshwari, S., *Acta Chim. Hung.*, 115, 3, 1984.
270. Grigor'ev, I. A., Mitasov, M. M., Shchukin, G. I., Korobeinicheva, I. K., and Volodarskii, L. B., *Zh. Org. Khim.*, 13, 1532, 1977.
271. Dugas, H. and Ptak, M., *Chem. Commun.*, p. 710, 1982.
272. Medzhidov, A. A., Rzaev, A. A., and Guseinova, M. K., *Koord. Khim.*, 11, 933, 1985.
273. Medzhidov, A. A., Mamedov, Kh. S., and Rzaev, A. A., *Koord. Khim.*, 11, 313, 1985.
274. More, K. M., Eaton, G. R., and Eaton, S. S., *J. Magn. Reson.*, 63, 151, 1985.
275. Grigor'ev, I. A. and Volodarskii, L. B., *Zh. Org. Khim.*, 11, 1328, 1975.
276. Dikanov, S. A., Shchukin, G. I., Grigor'ev, I. A., Rukin, S. I., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 565, 1985.
277. Larionov, S. V., Avdeeva, M. I., Ovcharenko, V. I., Grigor'ev, I. A., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 2797, 1983.
278. More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 24, 3820, 1985.
279. Martin, V. V., Vishnivetskaya, L. A., Grigor'ev, I. A., Dikanov, S. A., and Volodarskii, L .B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 1616, 1985.
280. Shchukin, G. I., Grigor'ev, I. A., and Volodarskii, L. B., *Izv. Sib. Otd. Akad. Nauk S.S.S.R. Ser. Khim. Nauk*, 4, 81, 1984.
281. Mamedova, Yu. G. and Tuarsheva, Z. O., *Zh. Org. Khim.*, 19, 1953, 1983.
282. Emanuel, N. M., Konovalova, N. P., D'yachkovskaya, R. F., and Denisova, L. K., *Antibiotiki*, 27, 811, 1982.
283. Mathew, A. E. and Cheng, C. C., *Tetrahedron Lett.*, 25, 269, 1984.
284. Solozhenkin, P. M., Shvengler, F. A., Kopitsya, N. I., and Semikopnyi, A. I., *Dokl. Akad. Nauk S.S.S.R.*, 262, 904, 1982.
285. Reznikov, V. A. and Volodarskii, L. B., *Tetrahedron Lett.*, p. 1301, 1986.
286. Tkacheva, O. P., Martin, V. V., Volodarskii, L. B., and Buchachenko, A. L., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 1153, 1981.
287. Amitina, S. A. and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 2135, 1976.
288. Oester, D. A. and Reinitz, D. M., *Fluorescein Hapten: An Immunological Probe*, Voss, E. W., Jr., Ed., CRC Press, Boca Raton, Fla., 1984, 183.
289. Lajzerowicz-Bonneteau, J., *Spin Labeling, Theory and Applications*, Berliner, L. J., Ed., Academic Press, New York, 1976, chap. 6.
290. Chion, B. and Zajzerowicz-Bonneteau, J., *Acta Cryst.*, B36, 998, 1980.
291. Ayscough, P. B., *Electron Spin Resonance in Chemistry*, Methuen, London, 1967, 282.
292. Bielsky, B. H. J. and Gebicki, J. M., *Atlas of Electron Spin Resonance Spectra*, Academic Press, New York, 1967, 379.
293. Antsiferova, L. I., Vasserman, A. M., Ivanova, A. N., Livshits, V. A., and Nazemets, N. S., *Atlas of Electron Spin Resonance Spectra of Spin Labels and Spin Probes* (in Russian), Nauka, Moscow, 1977.
294. Freed, J. H., *Spin Labeling, Theory and Applications*, Berliner, L. J., Ed., Academic Press, New York, 1976, chap. 3.
295. Janzen, E. G., *Methods Enzymol.*, 105, 188, 1984.
296. Kissler, K. D., Sheppard, S. K., Eaton, G. R., and Eaton, S. S., *J. Magn. Reson.*, 63, 74, 1985.
297. Dalal, D. P., Damoder, R., Benner, C., Eaton, G. R., and Eaton, S. S., *J. Magn. Reson.*, 63, 125, 1985.
298. Dalal, D. P., Damoder, R., Eaton, G. R., and Eaton, S. S., *J. Magn. Reson.*, 63, 327, 1985.
299. Wagner, B. E., Linowski, J. W., Potenza, J. A., Bates, R. D., Jr., Helbert, J. N., and Poindexter, E. H., *J. Am. Chem. Soc.*, 98, 4405, 1976.
300. Indrichan, K. M., Larionov, S. V., Gebreleu, N. V., and Ovcharenko, V. I., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 1664, 1985.
301. Boguslavskii, E. G., Shklyaev, A. A., Yudanov, V. F., Ovcharenko, V. I., and Larionov, S. V., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 1517, 1984.

302. Medzhidov, A. A. and Timakov, I. A., *Koord. Khim.*, 8, 1043, 1982.
303. Kokorin, A. I., Parmon, V. N., Ovcharenko, V. I., Larionov, S. V., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, p. 1763, 1981.
304. Grand, A., Rey, P., and Subra, R., *Inorg. Chem.*, 22, 391, 1983.
305. Laugier, J., Ramasseul, R., Rey, P., Espie, J. C., and Rassat, A., *Nouv. J. Chim.*, 7, 11, 1983.
306. Solozhenkin, P. M., Zelenov, V. I., Kopitsya, N. I., and Makeev, V. A., *Dokl. Akad. Nauk Tadzh. S.S.R.*, 25, 399, 1982.
307. Hafid, S., Eaton, G. R., and Eaton, S. S., *J. Magn. Reson.*, 51, 470, 1983.
308. Smith, P. H., Eaton, G. R., and Eaton, S. S., *J. Am. Chem. Soc.*, 106, 1986, 1984.
309. Al-Malaika, S., Kok, L., and Scott, G., *Polym. Commun.*, 25, 233, 1984.
310. Barashkova, I. I., Kovarskii, A. L., and Vasserman, A. M., *Vysokomolek. Soedin. A*, 24, 91, 1982.
311. Ovcharenko, V. I., Larionov, S. V., Mokhosoeva, V. K., and Volodarskii, L. B., *Zh. Neorg. Khim.*, 28, 151, 1983.
312. Ovcharenko, V. I., Larionov, S. V., Mironova, G. N., Patrina, L. A., Avdeeva, M. I., Boguslavskii, E. G., Grigor'ev, I. A., Shchukin, G. I., and Volodarskii, L. B., U.S.S.R. Natl. Conf. on Nitroxide Radicals, Abstracts, May 12 to 14, 1982, Chernogolovka, 1982, 11.
313. Ovcharenko, V. I., Ikorskii, V. N., and Larionov, S. V., Proc. 10th Conf. on Coordination Chemistry, Smolenice (Bratislava), 1985, 309.
314. More, K. M., Eaton, S. S., and Eaton, G. R., *J. Am. Chem. Soc.*, 103, 1087, 1981.
315. Solozhenkin, P. M., Shvengler, F. A., Semikopnyi, A. I., and Kopitsya, N. I., U.S.S.R. Author's Certificate No. 973540, 1982.
316. Solozhenkin, P. M., Semikopnyi, A. I., Rakitina, E. V., and Burichenko, V. K., *Dokl. Akad. Nauk S.S.S.R.*, 274, 88, 1984.
317. Solozhenkin, P. M., Shvengler, F. A., Kopitsya, N. I., and Ivanov, A. V., *Dokl. Akad. Nauk S.S.S.R.*, 269, 881, 1983.
318. More, K. M., Eaton, G. R., and Eaton, S. S., *Can. J. Chem.*, 60, 1392, 1982.
319. More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 22, 934, 1983.
320. Damoder, R., More, K. M., Eaton, G. R., and Eaton, S. S., *J. Am. Chem. Soc.*, 105, 2147, 1983.
321. Damoder, R., More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 22, 2836, 1983.
322. Damoder, R., More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 22, 3738, 1983.
323. More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 23, 1165, 1984.
324. Damoder, R., More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 23, 1320, 1984.
325. Damoder, R., More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 23, 1326, 1984.
326. More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 23, 4084, 1984.
327. Fielding, L., More, K. M., Eaton, G. R., and Eaton, S. S., *J. Am. Chem. Soc.*, 108, 618, 1986.
328. More, K. M., Eaton, G. R., and Eaton, S. S., *J. Magn. Reson.*, 60, 54, 1984.
329. Hata, S. and Tsuchida, E., *Kobunshi Ronbunshu*, 37, 635, 1980; Chem. Abstr. 94, 31183.
330. Eaton, S. S., More, K. M., Sawant, B. M., Boymel, P. M., and Eaton, G. R., *J. Magn. Reson.*, 52, 435, 1983.
331. Boymel, P. M., Chang, J. R., DuBois, D. L., Greenslade, D. J., Eaton, G. R., and Eaton, S. S., *J. Am. Chem. Soc.*, 99, 5500, 1977.
332. Boymel, P. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 19, 727, 1980.
333. Boymel, P. M., Braden, G. A., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 19, 735, 1980.
334. Sawant, B. M., Eaton, G. R., and Eaton, S. S., *J. Magn. Reson.*, 45, 162, 1981.
335. Sawant, B. M., Shroyer, A. L. W., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 21, 1093, 1982.
336. More, J. K., More, K. M., Eaton, G. R., and Eaton, S. S., *Inorg. Chem.*, 21, 2455, 1982.
337. Eaton, S. S., Boymel, P. M., Sawant, B. M., More, J. K., and Eaton, G. R., *J. Magn. Reson.*, 56, 183, 1984.
338. More, J. K., More, K. M., Eaton, G. R., and Eaton, S. S., *J. Am. Chem. Soc.*, 106, 5395, 1984.
339. More, K. M., Eaton, G. R., and Eaton, S. S., *J. Magn. Reson.*, 59, 497, 1984.
340. Ogiyama, S., Okada, K., Tajima, K., Sasaki, H., Mukai, K., and Ishizu, K., *Chem. Lett.*, p. 705, 1982.
341. Dickman, M. H. and Doedens, R. J., *Inorg. Chem.*, 22, 1591, 1983.
342. Schwarzhans, K. E. and Stuefer, A., *Monatsch. Chem.*, 114, 137, 1983.
343. Schwarzhans, K. E. and Stuefer, A., *Z. Naturforsch. B*, 36B, 195, 1981.
344. Cotton, F. A. and Felthouse, T. R., *Inorg. Chem.*, 21, 2667, 1982.
345. Solozhenkin, P. M., Shapiro, A. B., Shvengler, F. A., and Ivanov, A. V., *Dokl. Akad. Nauk S.S.S.R.*, 265, 137, 1982.
346. Dong, T. Y., Hendrickson, D. N., Felthouse, T. R., and Shieh, H. S., *J. Am. Chem. Soc.*, 106, 5373, 1984.
347. Bilgrien, C., Drago, R. S., Stahlbush, J. R., and Kuechler, T. C., *Inorg. Chem.*, 24, 4268, 1985.

348. Dickman, M. H. and Doedens, R. J., *Inorg. Chem.*, 20, 2677, 1981.
349. Drago, R. S., *Coord. Chem. Rev.*, 32, 97, 1980.
350. Anderson, O. P. and Kuechler, T. C., *Inorg. Chem.*, 19, 1417, 1980.
351. Eaton, S. S., Law, M. L., Peterson, J., Eaton, G. R., and Greenslade, D. J., *J. Magn. Reson.*, 33, 135, 1979.
352. Tsukerblat, B. S., Fung Min Shon, *Izv. Akad. Nauk Mold. S.S.R. Ser. Biol. Khim. Nauk*, 2, 50, 1984.
353. Dalal, D. P., Eaton, S. S., and Eaton, G. R., *J. Magn. Reson.*, 44, 415, 1981.
354. Sarna, T. and Lukiewicz, S., *Folia Histochem. Cytochem.*, 9, 203, 1971.
355. Poole, C. P., *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques*, 2nd ed., John Wiley & Sons, New York, 1983.
356. Fitzky, H. G., *Analytiker-Taschenbuch*, Band 4, Herausgeber: W. Fresenius, Akademie-Verlag, Berlin, 1984, S. 181.
357. Chang, T.-T., *Magn. Reson. Rev.*, 9, 65, 1984.
358. Slangen, H. J. M., *J. Phys.*, 3, 775, 1970.
359. Warren, D. C. and Fitzgerald, J. M., *Anal. Chem.*, 49, 1840, 1977.
360. Molin, Yu. N., Chibrikin, V. M., Shabalkin, V. A., and Shuvalov, V. F., *Zav. Lab.*, 32, 933, 1966.
361. Nakano, K., Tadano, H., and Sugimoto, S., *Nippon Kagaku Kaishi*, p. 885, 1979.
362. Wilmshurst, T. H., *Electron Spin Resonance Spectrometers*, Hilger, London, 1967.
363. Solozhenkin, P. M., Shalukhina, L. M., Zinchenko, Z. A., Shvengler, F. A., and Usova, S. V., *Dokl. Akad. Nauk Tadzh. S.S.R.*, 26, 232, 1983.
364. Wasson, J. R., *Anal. Chem.*, 58, 81R, 1986.
365. Nagy, V. Yu., Grazhulene, S. S., Petrukhin, O. M., Zolotov, Yu. A., and Volodarskii, L. B., *Izv. Akad. Nauk S.S.S.R. Ser. Khim.*, in press.
366. Hinze, J. and Jaffe, H. H., *J. Am. Chem. Soc.*, 84, 540, 1962.
367. Hinze, J., Whitehead, M. A., and Jaffe, H. H., *J. Am. Chem. Soc.*, 85, 148, 1963.
368. Huheey, J. E., *J. Org. Chem.*, 31, 2365, 1966.