

Direct Electrochemical Synthesis of the Chelates of a Novel Ligand: Salicylhydrazone of 2-(N-tosylamino)benzaldehyde

L.M. Blanco* and
B.I. Kharisov
Facultad de Ciencias Químicas
Universidad Autónoma
de Nuevo León
San Nicolás de los
Garza, N.L. 66450 México
Fax: (52-8)3753846
E-mail: leoblanco@hotmail.com

A.S. Burlov, A.D. Garnovskii,
L.I. Kuznetsova and
I.S. Vasilchenko
Institute of Physical &
Organic Chemistry
Rostov State University
Rostov-on-Don 344006 Russia
Fax: (7-8632)285667
E-mail: garn@ipoc.rnd.runnet.ru

*corresponding author

The interaction of a new ligand system, salicylhydrazone of 2-(N-tosylamino)-benzaldehyde (LH₃), with elemental cobalt, copper and zinc (electrochemical synthesis) or their acetates (conventional chemical synthesis) leads to the chelates [M₃L₂]_n (M=Co,Cu) or [Zn(LH)]₂. On the basis of IR and ¹H NMR spectroscopy and magnetochemistry data the structures of di- and trimeric complexes are discussed in this paper.

The theory of coordination chemistry gives great importance to metallic complexes obtained from inorganic or organic ligands with an N atom in the molecule. In particular, azomethinic ligands of the type I (**F1**), which contain a C=N- bond with an sp²-hybridized N atom, have been intensively studied over the last 30 years.

The goal of synthetic work in this area has been to produce different kinds of metal complexes starting from the same ligand. Different complexes may arise as a consequence of the presence of an intramolecular hydrogen bond, a tautomeric equilibrium between ketoenol (thione-thiol) and iminoamine forms, or of the molecular spatial configurations (substitution patterns) summarized in **F1**.

Thus, two broad classes of coordination compounds can be obtained: adducts (molecular complexes) with a conserved ligand system, and

chelates with a deprotonated azomethinic group containing intrachelate bonds. Depending on the nature of the metal and anion, as well as the synthetic conditions, either an adduct or a chelate is obtained.

In the ligand I systems (**F1**), it is possible to obtain rings containing six members with an intra-molecular hydrogen bond, which gives the possibility of obtaining the corresponding metal chelates with six membered rings.

The chelates of azomethinic derivatives of 2-(N-tosylamino)benzaldehyde (**Ia**) are not very common (1-7), in contrast to similar ligands of the salicylaldehyde series **Ib** (8-13) (**F1**). For this reason, it is interesting to obtain and characterize metal chelates on the basis of this new system, specifically involving the **III** ligand (LH₃) shown in **F2**.

In this paper the direct electrochemical synthesis of the metallic chelates [M₃L₂]_n (M=Co,Cu) or

[Zn(LH)]₂ from a new ligand system—salicylhydrazone of 2-(N-tosylamino)-benzaldehyde (**F2**)—is reported, and the products are compared with those synthesized using conventional chemical methods. On the basis of IR and ¹H NMR spectroscopy and magnetochemistry data, the structures of di- and trimeric complexes are also discussed.

Experimental Procedures

Materials and Equipment

Metals and LiClO₄ (Aldrich) were used as supplied. Methanol was purified by a standard method. The electrosyntheses were carried out using a power supply PS 500-1 (Sigma Aldrich). Metal contents were determined by the atomic absorption method. C,H,N contents were determined by standard methods of organic analysis on a Carlo-Erba 1108 microanalyzer. IR and ¹H NMR spectra were recorded on a Perkin-

Elmer spectrophotometer and on a Bruker DPX 400 spectrometer (125 MHz, 298 K, with Me₄Si as an internal reference and DMSO-d₆ as a solvent), respectively. The determination of magnetic properties was carried out by Faraday's method at 80-300 K (14). The diamagnetic susceptibility χ_d was calculated according to the Pascal method (15). The polarization magnetism N_α was accepted to be $60 \times 10^{-6} \text{ cm}^3/\text{mol}$ per copper atom.

Ligand Synthesis

Salicylhydrazone of 2-(N-tosylamino)benzaldehyde was synthesized as reported in the literature (2). Briefly, a methanol solution (20 mL) of salicylhydrazide (1.52 g, 10^{-3} mol) was added to a methanol solution (50 mL) of 2-(N-tosylamino)benzaldehyde (2.75 g, 10^{-3} mol) (16). This mixture was heated at reflux for two hours. After cooling, the sediment was isolated, filtered and recrystallized from methanol (yield: 90%).

Metal Complexes

The metal complexes were obtained as follows:

Conventional chemical synthesis. A methanol solution (30 mL) of each metal (Co, Cu or Zn) acetate (10^{-3} mol) was added to a methanol solution (30 mL) of an equimolar amount of the salicylhydrazone of 2-(N-tosylamino)benzaldehyde. The mixture was heated at reflux for one hour in a water bath. The solids formed were filtered, washed three times with 5 cm³ of methanol and dried *in vacuo* at 150 °C (yield: 75-80%).

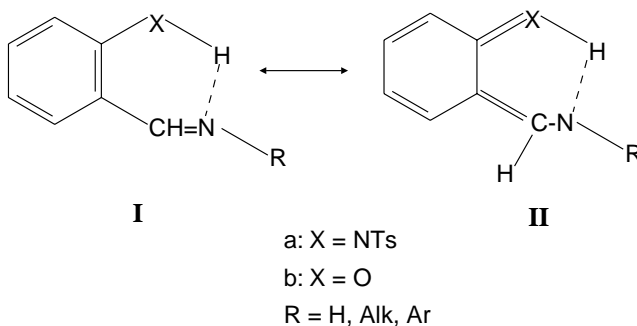
Electrochemical synthesis (17-19). The electrochemical cell consisted of a tall-form beaker, and the solution phase contained the ligand (10^{-3} mol) and LiClO₄ (0.01 N) dissolved in methanol (30 mL) as a supporting electrolyte. A metal sheet was used as the anode and a platinum sheet formed the cathode. The electrolysis was conducted at a current of 20 mA and a voltage of 20-30 V for four hours at room temperature. The electrochemical cell can be schematically represented by:

Pt(-)/ligand, CH₃OH/M(+)
(M = Co, Cu, Zn)

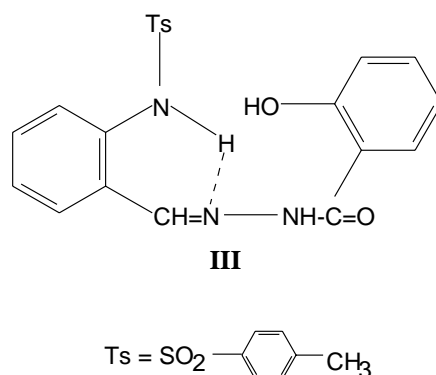
The resulting complexes were filtered, washed three times with 5 cm³ of methanol and dried *in vacuo* at 150 °C (yield: 90-95%).

The corresponding elemental analysis data are presented in **T1**.

F1



F2



T1

Elemental analysis and related data of salicylhydrazone of 2-(N-tosylamine)benzaldehyde (I) and its complexes.

No.	Compos.	M.P. (°C)	C	H	% (f/c)** N	M	S	Formula
III	H ₃ L	209-210	f: 61.40 c: 61.60	4.90 4.68	10.95 10.26	— —	7.95 7.83	C ₂₁ H ₁₁ N ₃ O ₄ S
IVa	Co ₃ L ₂	>250	f: 51.12 c: 50.97	3.15 3.26	8.25 8.49	17.98 17.86	6.21 6.48	C ₄₂ H ₃₂ N ₆ O ₈ S ₂ Co ₃
IVb	Cu ₃ L ₂	>250	f: 50.92 c: 50.28	3.57 3.18	8.64 8.37	18.72 19.00	6.50 6.39	C ₄₂ H ₃₂ N ₆ O ₈ S ₂ Cu ₃
IVb*	Cu ₃ L ₂	>250	f: 51.02 c: 50.28	3.49 3.18	9.08 8.37	18.64 19.00	6.50 6.39	C ₄₂ H ₃₂ N ₆ O ₈ S ₂ Cu ₃
V	[Zn(HL)] ₂	>250	f: 53.66 c: 53.34	3.90 3.62	9.02 8.89	14.07 13.83	6.36 6.78	(C ₂₁ H ₁₇ N ₃ O ₄ SZn) ₂
V*	[Zn(HL)] ₂	>250	f: 53.70 c: 53.34	3.42 3.62	9.10 8.89	13.75 13.83	6.80 6.78	(C ₂₁ H ₁₇ N ₃ O ₄ SZn) ₂
VI	Cu ₃ L ₂ Py ₂	>250	f: 53.17 c: 53.77	4.09 3.62	9.20 9.64	16.70 16.42	5.72 5.52	C ₅₂ H ₄₂ Cu ₃ N ₆ O ₈ S ₂

* Complexes obtained electrochemically.

** f: found, c: calculated.

Results and Discussion

The IR data (amide carbonyl band at 1633 cm^{-1} and azomethinic band at 1606 cm^{-1}) and ^1H NMR spectra (NH 10.97 ppm, Ts-NH 11.83 ppm, N=CH 8.52 ppm, O-H \cdot O=C 12 ppm) testify to the existence of a tautomeric equilibrium for

Ia (F1). This kind of equilibrium is also typical for other azomethinic ligands (2,10,11,20,21), in which form **I** predominates (22). The ^1H NMR spectrum of the hydrazone fragment coincides with the data reported in the literature (23).

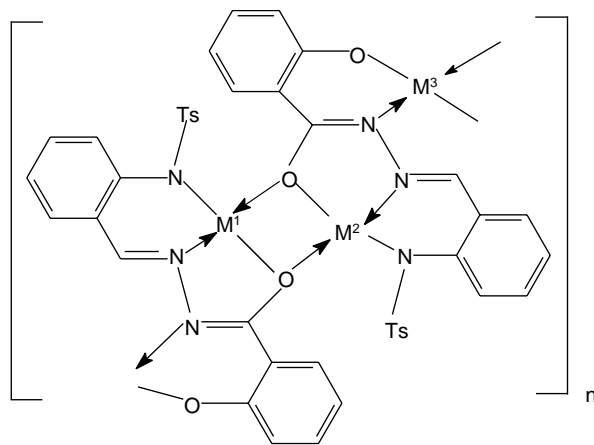
Some types of complexes, including di- and trinuclear structures

(3,6), can be obtained on the basis of the polydentate ligand **III (F2)**. Moreover, the chelates containing an acetate group are formed as a result of a conventional chemical synthesis from $\text{M}(\text{Ac})_2$ (Ac = OCOMe \cdot). The complexes without an acetate group are obtained by electro-synthesis from elemental metals (19,24-27).

The elemental analysis data (**T1**) are consistent with the fact that chelates $[\text{M}_3\text{L}_2]_n$ (M=Co,Cu) and $[\text{Zn}(\text{LH})]_2$ (LH $_3$ = **III**) can be obtained by both chemical and electro-chemical synthesis methods.

The structures of the resulting products will now be discussed on the basis of spectral (Zn complexes) and magnetochemical (Cu complexes) data. The intense amide carbonyl band at 1633 cm^{-1} disappears upon complexation, and bands at $1606\text{--}1616\text{ cm}^{-1}$ are observed; these bands could be attributed to valence oscillations of the azomethinic coordinated bond by the N-atom (28). In the case of the copper chelates, the bands of OH and NH groups (3159 and 3356 cm^{-1} , respectively) disappear (**T2**). On the other hand, a band

F3



IV

a: M = Co
b: M = Cu

T2

IR spectral data of ligands and metal complexes.

No.	n(OH) cm^{-1}	n(NH) cm^{-1}	n(C=O) cm^{-1}	n(C=N) cm^{-1}	n _{as} (SO $_2$) cm^{-1}	n _s (SO $_2$) cm^{-1}
III	3356 w	3159 w	1633 vs	1606 s	1327 vs	1147 vs
IVa	–	–	–	1610 vs 1593 vs	1280 s	1128 vs
IVb	–	–	–	1608 vs, 1593 vs	1273 s	1126 vs
IVb*	–	–	–	1608 s, 1593 s	1273 s	1126 vs
V	3204 w	–	–	1616 s, 1586 s	1260 s	1113 vs
V*	3205 w	–	–	1615 s, 1587 s	1262 s	1113 vs
VI	–	–	–	1593 s	1274 s	1124 vs

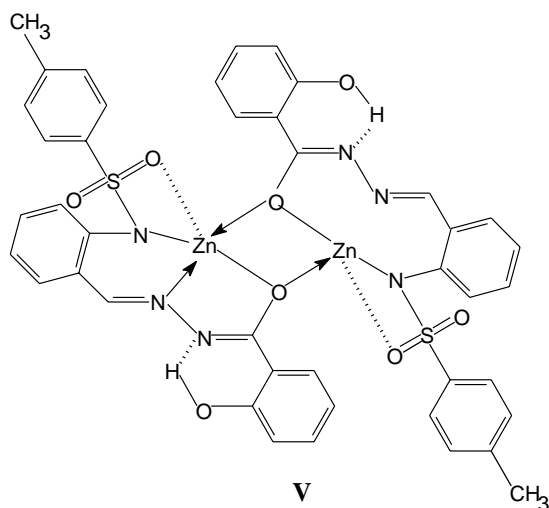
*Complexes obtained electrochemically.

T3

Magnetic properties of copper complexes (m_{eff} /copper atom).

T3a. Compound: IVb $g = 2.13, J_1 = -45\text{ cm}^{-1}, J_2 = -188\text{ cm}^{-1}, r = 1.47$										
T, K	82.6	86.5	91.8	99.6	128.5	141.0	185.5	245.0	285.0	299.3
$M'_{\text{eff}}^{\text{exp}}$, B.M.	1.09	1.09	1.08	1.11	1.12	1.15	1.25	1.35	1.42	1.42
$M'_{\text{eff}}^{\text{teor}}$, B.M.	1.09	1.09	1.09	1.10	1.13	1.15	1.25	1.35	1.42	1.44
T3b. Compound: VI $g = 2.25, J_1 = -39\text{ cm}^{-1}, r = 2.38$										
T, K	80.0	86.0	100.0	141.0	152.0	180.0	197.0	224.0	246.0	287.0
$M'_{\text{eff}}^{\text{exp}}$, B.M.	1.44	1.47	1.54	1.70	1.72	1.76	1.80	1.83	1.84	1.85
$M'_{\text{eff}}^{\text{teor}}$, B.M.	1.46	1.49	1.56	1.68	1.70	1.75	1.77	1.80	1.82	1.85

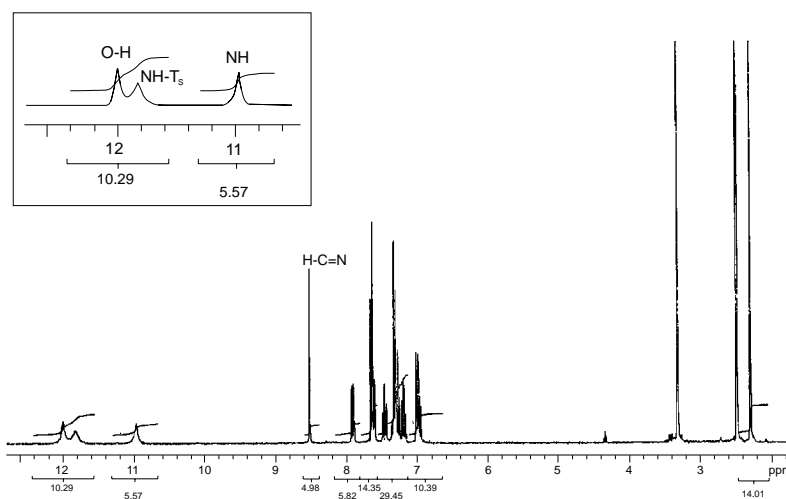
F4



of low intensity at $\approx 3200\text{ cm}^{-1}$ is observed in the spectrum of the zinc complex obtained in both the chemical and electrochemical syntheses. This can be attributed to valence oscillations of the OH group, which takes part in the formation of a hydrogen bond with the nitrogen atom of the C=N fragment (29). These results testify that a complete deprotonation of the ligand system LH_3 takes place in the copper complex; thus, three hydrogen atoms are replaced by metal (**IV**) (**F3**), but, in the case of the zinc complex, one hydrogen atom remains (**V**) (**F4**).

F5

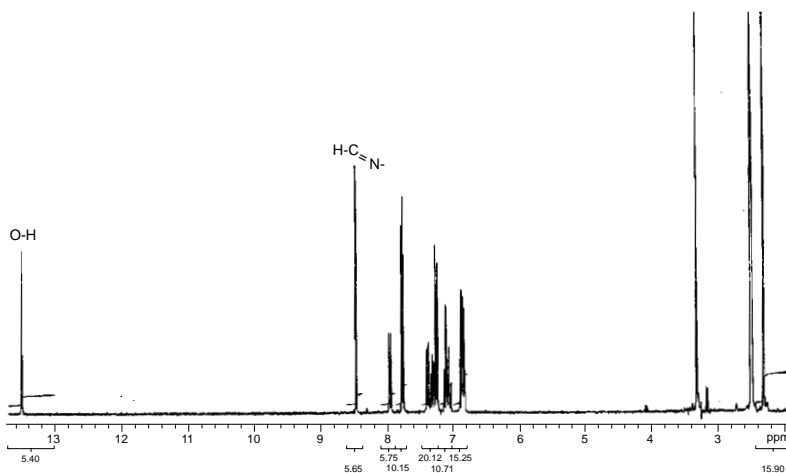
Spectrum for the ligand **III** (**F2**).



Additional evidence supporting structure **V** was obtained by a comparative study of ^1H NMR spectra of the ligand **III** (**F2**) and the complex **V**. Of note are the following: for structure **V**: 2.30 ppm (s, 3H, CH_3), 6.83-6.90 ppm (m, 3H, $\text{H}_{\text{arom.}}$), 7.03-7.11 ppm (m, 2H, $\text{H}_{\text{arom.}}$), 7.23-7.37 ppm (m, 4H, $\text{H}_{\text{arom.}}$), 8.46 ppm (s, 1H, $\text{N}=\text{CH}$), 13.5 ppm (w.s., 1H, OH). In contrast to the spectrum of the ligand **III** (**F5**), which contains peaks for the NH and OH groups (30), only one peak (13.5 ppm, OH fragment) is observed in this region of the spectrum for the zinc complex **V** (**F6**). Moreover, an HC=N group peak (8.50 ppm (30)) is also present.

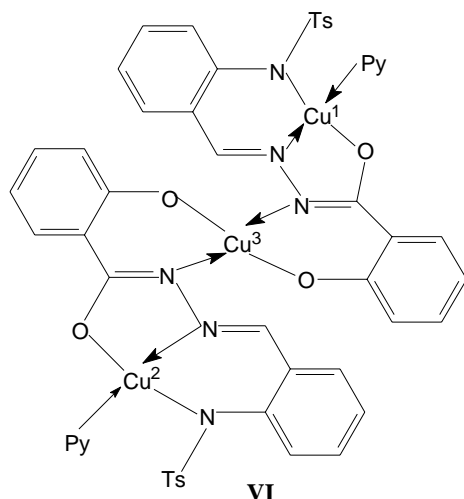
F6

Spectrum for the zinc complex **V** (**F4**).



Although the formation of dimers (**V**) has not strictly been proved in the present work, their existence is certainly possible taking into account that many similar structures are present in various hydrazone complexes (31-33). According to X-ray diffraction data (33,34), a dimer structure containing the Zn_2O_2 bridge exists in the zinc complex of the thioacylhydrazone of salicylic aldehyde. The zinc atom in **V** is pentacoordinate due to O-atoms of DMSO, which was used as a solvent.

To confirm structures of the copper complexes, their magnetic properties were studied over the temperature range 80-300 K. The results show that the magnetic properties of the copper chelates $[\text{Cu}_3\text{L}_2]_n$ are practically the same, independent of the preparation method used. The magnitudes of the effec-



tive magnetic moments ($\mu_{\text{eff.}}$) calculated for each copper atom are lower (1.42 B.M.) than those corresponding to pure spin, and decrease with the reduction of temperature (**T3**). Such a temperature dependence of $\mu_{\text{eff.}}$ is undoubtedly related to an antiferromagnetic exchange interaction between copper atoms. The exchange parameters were calculated for the three-nuclear fragment according to (35). Exchange interaction constants in fragment **IVb** (**F3**) between copper atoms $\text{Cu}^1\text{-Cu}^3$ and $\text{Cu}^2\text{-Cu}^3$ ($J_1 = -45 \text{ cm}^{-1}$) are considerably lower (absolute magnitude) than those for $\text{Cu}^1\text{-Cu}^2$ ($J_2 = -188 \text{ cm}^{-1}$). This is probably related to the fact that the exchange is carried out through a conjugated system in the first case, and through bridging oxygen atoms in the second case.

The studied copper complexes were recrystallized from pyridine (Py). It is known from the majority of reported data (8,36) that the interaction of dimer and polymer structures having a M_2O_2 bridge and N-bases of an azine type leads to monomer adduct formation. However, the elemental analysis data (compound **VI**, **T1**) and the variation of magnetochemical properties with temperature are consistent with the conclusion that the isolated adduct has the composition $\text{Cu}_3\text{L}_2\text{Py}_2$ and the structure **VI** (**F7**).

The trimer **VI** has antiferromagnetic properties; however, the magnitude of its exchange interaction is lower than that of complex **IVb** (**F3**). This apparent contradiction can be explained by the increase in the $\text{Cu}^1\text{-Cu}^2$ distance in chelate **VI** as compared to that in the trinuclear compound **IVb**.

Conclusions

Chelates from the new ligand 2-(N-tosylamine)-benzaldehyde were obtained. The structures $[\text{M}_3\text{L}_2]_n$ ($\text{M}=\text{Co}, \text{Cu}$) and $[\text{Zn}(\text{LH})]_2$ were deduced for these chelates from spectroscopic analysis and magnetochemical data. They were obtained by both conventional chemical and direct electrochemical synthesis methods.

The direct electrochemical synthesis using elemental metals as sacrificial anodes (37) gave higher yields (90-95%) than those obtained with traditional methods using metal acetates (75-80%).

References

1. A.D. Garnovskii, V.A. Alexeenko, V.A. Kogan, B.M. Bolotin, O.A. Osipov, T.A. Yusman, and N.I. Chernova, *Koord. Khim.* 3 (1977) 500.
2. A.S. Burlov, A.D. Garnovskii, V.A. Alexeenko, A.E. Mistryukov, V.S. Sergienko, V.G. Saletov, V.V. Lukov, A.V. Khoklov, and M.A.

- Porai-Koshitz, *Koord. Khim.* 18 (1992) 859.
3. A.D. Garnovskii, A.S. Burlov, V.V. Lukov, V.G. Saletov, O.T. Asmaev, S.I. Levchenkov, E.G. Amarskii, and D.A. Garnovskii, *Koord. Khim.* 22 (1996) 838.
4. A.D. Garnovskii, A.S. Burlov, D.A. Garnovskii, I.S. Vasil'chenko, A.S. Antsyshkina, G.G. Sadikov, A. Sousa, J.A. García-Vázquez, and J. Romero, *Koord. Khim.* 23 (1997) 399.
5. B.I. Kharisov, L.M. Blanco, A.D. Garnovskii, A.S. Burlov, L.I. Kuznetsova, L.I. Korovina, D.A. Garnovskii, and T. Dieck, *Polyhedron* 17 (1998) 381.
6. J.A. García-Vázquez, J. Romero, M.L. Durán, A. Sousa, A.D. Garnovskii, A.S. Burlov, and D.A. Garnovskii, *Polyhedron* 17 (1998) 1547.
7. B.I. Kharisov, D.A. Garnovskii, L.M. Blanco, A.S. Burlov, I.S. Vasil'chenko, and A.D. Garnovskii, *Polyhedron* (in press).
8. R.H. Holm, G.W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.* 7 (1966) 83.
9. G.V. Panova, N.K. Vikulova, and W.M. Potapov, *Usp. Khim.* 49 (1980) 1234.
10. M. Calligaris and L. Randaccio in "Comprehensive Coordination Chemistry" Vol. 2 (G. Wilkinson, Ed.), Pergamon Press, Oxford, 1987, 715.
11. A.D. Garnovskii, A.L. Nivorozhkin, and V.I. Minkim, *Coord. Chem. Rev.* 126 (1996) 1.
12. A.D. Garnovskii, D.A. Garnovskii, A.S. Burlov, and I.S. Vasil'chenko, *Mendeleev Chem. J. (Zhurn. Ros. Khim. Ob-va im. D.I. Mendeleeva)* 40(4-5) 1996 19.
13. A.D. Garnovskii, *Zhurn. Neorg. Khim.* 43 (1998) 1377.
14. V.P. Kurbatov, A.V. Khokhlov, A.D. Garnovskii, O.A. Osipov, and L.A. Khulkhatsieva, *Koord. Khim.* 5 (1979) 351.
15. P.W. Selwood, "Magnetochemistry," Interscience Publ., JNC, New York, 1956.
16. N.I. Chernova, Y.S. Rjabpkobilko, V.G. Brudz', and B.M. Bolotin, *Zhurn. Organ. Khim.* 8 (1971) 1680.
17. N.N. Bogdashev, A.D. Garnovskii, O.A. Osivop, V.P. Grigor'ev, and N.M. Gontmacher, *Zhurn. Obshch. Khim.* 46 (1976) 675.
18. J.J. Habeeb, D.G. Tuck, and E.H. Walters, *J. Coord. Chem.* 8 (1978) 27.
19. E. Labisbal, J.A. García-Vázquez, J. Romero, A. Sousa, A. Castiñeiras, C. Maichle-Mosser, and U. Russo, *Inorg. Chim. Acta* 223, 87.

20. V.A. Bren', and V.I. Minkin, *Isv. Vyssh. Uchebn. Zaved., Khim. Teknol.* 25 (1982) 663.
21. J. Costamagna, J. Vargas, R. Latorre, A. Alvarado and G. Mena, *Coord. Chem. Rev.* 119 (1992) 67.
22. A.S. Burlov, L.I. Kuznetsova, S.I. Adamova, V.P. Kurbatov, G.I. Bondarenko, and A.D. Garnovskii, *Zhurn. Obshch. Khim.* 1999 (in press).
23. K.K. Narang, and M.K. Sing, *Inorg. Chim. Acta* 131 (1987) 241.
24. D.G. Tuck, *Pure Appl. Chem.* 51 (1979) 2005.
25. D.G. Tuck in "Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds," Kluwer, Dordrecht, 1993, 15.
26. M.S. Chakravorty and G.V.P. Subrahmanyam, *Coord. Chem. Rev.* 135-136(1) (1994) 65.
27. A.D. Garnovskii, B.I. Kharisov, G. Gójon-Zorrilla, and D.A. Garnovskii, *Russ. Chem. Rev.* 64(3) (1995) 201.
28. P. Glushinskii, G.M. Mockler, and E. Sinn, *Spectrochim. Acta* 33A (1977) 1073.
29. L.J. Belamy, "Advances in Infrared Group Frequencies," Bungay, Suffolk, 1968.
30. D.A. Garnovskii, A.S. Burlov, A.D. Garnovskii, I.S. Vasil'chenko, and A. Sousa, *Zhurn. Obshch. Khim.* 66 (1996) 1546.
31. N.S. Biradar, V.B. Mahale, and B.R. Havinale, *Rev. Roum. Chim.* 23 (1978) 55.
32. V.A. Kogan, V.V. Zelentsov, G.M. Larin, and V.V. Lukov, "Complexes of Transition Metals with Hydrazones," Nauka, Moscow, 1990, 122.
33. V.A. Kogan and V.V. Lukov, *Koord. Khim.* 19 (1993) 476.
34. V.G. Yusupov, M.T. Toshev, and K.N. Zelenin, *Dep. in VINITI, No. 4188-B9*, 1989.
35. V.T. Kalinnikov and Y.V. Rakitin, "Introduction to Magnetochemistry. Method of Statistic Magnetic Susceptibility in Chemistry," Nauka, Moscow, 1980, 302.
36. A.S. Burlov, A.S. Antsyshkina, J. Romero, D.A. Garnovskii, J.A. García-Vázquez, A. Sousa, and A.D. Garnovskii, *Zhurn. Neorg. Khim.* 10 (1995) 1005.
37. "Direct Synthesis of Coordination and Organometallic Compounds" (A.D. Garnovskii and B.I. Kharisov, Eds.), Elsevier Science, in press.