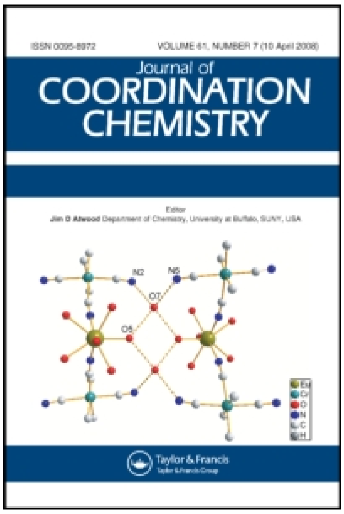


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

METAL CHELATES OF NEW LIGANDS: 1,2-BENZOTHIAZINE-1,1-DIOXIDE DERIVATIVES

A. V. Bicherov[a]; B. I. Kharisov[b]; L. M. Blanco[b]; O. Yu. Korshunov[a]; E. L. Koroleva[a]; A. S. Burlov[a]; G. S. Borodkin[a]; V. P. Kurbatov[a]; I. E. Uflyand[a]; A. D. Garnovskii[a]
[a] Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don, Russia [b] Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, México, C.P.

To cite this Article Bicherov, A. V. , Kharisov, B. I. , Blanco, L. M. , Korshunov, O. Yu. , Koroleva, E. L. , Burlov, A. S. , Borodkin, G. S. , Kurbatov, V. P. , Uflyand, I. E. and Garnovskii, A. D.(2001) 'METAL CHELATES OF NEW LIGANDS: 1,2-BENZOTHIAZINE-1,1-DIOXIDE DERIVATIVES', Journal of Coordination Chemistry, 54: 3, 337 — 342

To link to this Article: DOI: 10.1080/00958970108022646

URL: http://dx.doi.org/10.1080/00958970108022646

J. Coord. Chem., 2001, Vol. 54, pp. 337-342
Reprints available directly from the publisher
Photocopying permitted by license only

METAL CHELATES OF NEW LIGANDS: 1,2-BENZOTHIAZINE-1,1-DIOXIDE DERIVATIVES

A. V. BICHEROV[a], B. I. KHARISOV[b,*], L. M. BLANCO[b],
O. YU. KORSHUNOV[a], E. L. KOROLEVA[a], A. S. BURLOV[a],
G. S. BORODKIN[a], V. P. KURBATOV[a], I. E. UFLYAND[a]
and A. D. GARNOVSKII[a,†]

[a]*Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don, 344006, Russia;* [b]*Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N.L., A.P.18-F, C.P. 66450, México*

(Received 27 October 2000; In final form 28 February 2001)

The novel chelates ML_2 (M = Co, Ni, Cu, Zn) were obtained by the interaction of 3-benzoyl-4-hydroxy-1,2-benzothiazine-4(3H)-on-1,1-dioxide and 2-methyl-3-benzoyl-4-hydroxy-1,2-benzothiazine-4(3H)-on-1,1-dioxide with elemental metals (direct electrochemical synthesis) or their acetates (chemical synthesis) in methanol. The tetrahedral or polymeric-octahedral structures with a β-diketonate fragment are assigned based on IR and ^{1}H NMR spectra. The studied ligands and their complexes are model compounds of molecules used as anti-inflammatory drugs.

Keywords: Piroxicam; Isoxicam; 1,2-benzothiazine-3-carboxamide-1,1-dioxide; Complexes; Electrosynthesis; Ambidentate ligand system

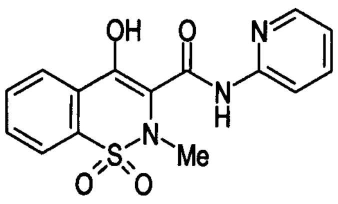
INTRODUCTION

Metal complexes of 1,2-benzothiazine-3-carboxamide-1,1-dioxide, for example those of piroxicam *1* and isoxicam *2*, are of permanent interest [1, 3]. These compounds are able to reduce the ulcerogenic effect of a series of anti-inflammatory medicines.

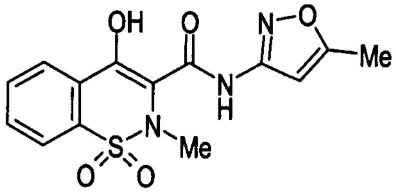
---

*Corresponding author. Tel.: 52 8 3753068, Fax: (52-8)3753846, e-mail: bkhariss@ccr.dsi.uanl.mx

†Fax: (7-8632)285667, e-mail: garn@ipoc.rsu.ru

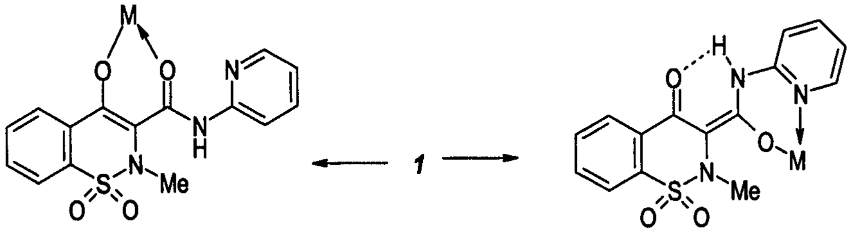


1



2

The ambidentate ligand system *1* [5, 6] allows formation of various types of metal cycles in its chelates, for example *3* or *4*:

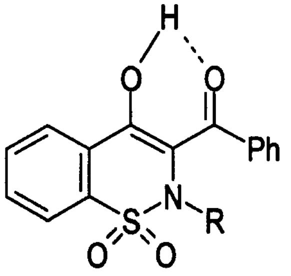


3

4

Complexes, obtained on the basis of the ligands *1* and *2*, have been reported [1, 3]. In particular, formation of the structure *4* with coordination MN_2O_2 was proposed for cadmium and copper complexes of piroxicam [3].

To examine ambident character of such ligands, we have synthesized the model compounds *5* and *6* and studied their complex-formation properties in the conditions of conventional chemical and direct electrochemical synthesis.



5 (R=H) or **6** (R=Me)

EXPERIMENTAL

Synthesis of the Ligands

3-Benzoyl-4-hydroxy-1,2-benzothiazine-4(3H)-on-1,1-dioxide (*5*, R = H) and 2-methyl-3-benzoyl-4-hydroxy-1,2-benzothiazine-4(3H)-on-1,1-dioxide (*6*, R = Me) were prepared according to the described method [7]. The melting points and characteristic bands in IR spectra of the products correspond to the reported data.

Chemical Synthesis of the Complexes (Method A)

The metal chelates were prepared by boiling methanol solutions of ligands *5* and *6* (0.01 mol) and cobalt, nickel, copper, and zinc acetates (0.005 mol), during several minutes. The formed solids were filtered, washed with cold methanol and dried in air. The yields of the products are the following: *7* – Co (60%), Ni (45%), Cu (70%), Zn (75%); *8* – Co (65%), Ni (40%), Cu (80%), Zn (78%).

Electrochemical Synthesis (Method B)

Methanol solutions (30 mL) of ligands *5* and *6* (0.002 mol) and Et_4NClO_4 (0.010 g) were introduced into an electrochemical cell. Corresponding metal (Zn, Cu, Co, Ni) was used as anode and a platinum sheet as cathode. The electrolysis was carried out at 40 mA and initial voltage 30 V during two (Zn) and three (Cu, Co, Ni) hours at room temperature. The formed solids were filtered, washed with cold methanol and dried in air. The yields of the products are the following: based on the weight of the ligand Co (36%), Ni (21%), Cu (17%), Zn (85%).

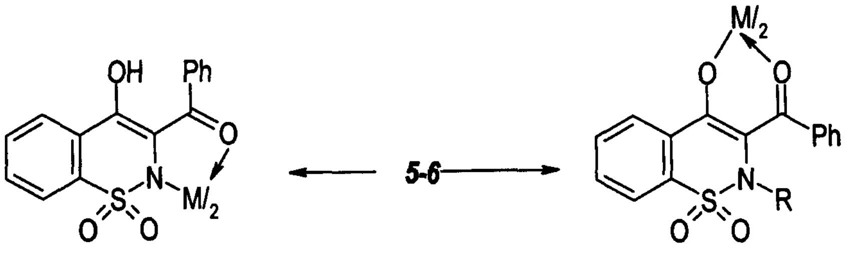
^1H NMR spectra (d_6-DMSO) were registered in the radiospectrometer UNITY-300 (Varian). The ligand *5* (3-benzoyl-4-hydroxy-1,2-benzothiazine-4(3H)-on-1,1-dioxide): 7.50–8.25 (m., 9, arom.), 9.73 (s., 1, NH), 15.80 (s. (broad.), 1, OH). The ligand *6* (2-methyl-3-benzoyl-4-hydroxy-1,2-benzothiazine-4(3H)-on-1,1-dioxide): 2.62 (s., 3, CH_3), 7.50–8.25 (m., 9, arom.), 15.78 {s. (broad.), 1, OH}. The complex *7* (R = H, M = Zn): 7.25–8.25 (m., 9, arom.), 9.78 (s., 1, NH). The complex *8* (R = Me, M = Zn): 2.21 (s., 3, CH_3), 7.25–8.20 (m., 9, arom.).

IR spectra of all obtained complexes (in vaseline oil) were recorded on a Specord IR-75 (see **Results and Discussion**). Magnetic properties of the products were studied by the Faraday method in solid phase at room temperature.

RESULTS AND DISCUSSION

The complexes, prepared by either conventional chemical or direct electrochemical methods have the same composition: ML_2, IR- and NMR-spectral and magnetochemical characteristics.

The ambidentate ligand *5* can result in two types of chelates *7* and *9*. In case of *6*, only chelates with β-diketonate coordination *8* can be obtained.



9

7 (R=H) or **8** (R=Me)

The absorption bands, characteristic of the enol form of a β-diketonate fragment (1593, 1606 cm^{-1}) [8] and containing an intra-molecular hydrogen bond ($\sim$3200–3300 cm^{-1}) [9, 10] are present in IR spectra of the ligands *5* and *6*. The oscillations of SO_2-group [8] correspond to the bands 1310, 1150, 580, 530 cm^{-1}. Moreover, a narrow band 3260 cm^{-1}, typical for secondary sulfamides, is observed for the compound with a free NH-group.

The bands 3200–3300 m^{-1} of valence oscillations of the OH group of a β-diketonate fragment (structure *8*) disappear in IR spectra of the complexes, obtained from *6*. Analogous changes are also observed in IR spectra of complexes of ligand *5*. However, only two bands (3200 and 3460 cm^{-1}) of the NH fragment of the sulfamide group are observed in the area of the LiF prism.

Confirmation of structure *7* for ligand *5* was also obtained as a result of comparison of ^1H NMR spectra of the ligand and its zinc complex. The spectra of *5* contain shifts of NH- and OH-protons at 9.73 and 15.80 ppm, respectively. Only the OH signal disappears in the zinc complex, indicating structure *7*. The ^1H NMR spectra of the ligand *6* contain a signal of the OH-proton in the area of 16.00 ppm, which is absent in the spectra of zinc complex of this ligand.

The magnetic measurements (Tab. I) show that the metals have the same oxidation state (+2) in the complexes obtained by different routes (A and B). The magnitudes of magnetic moments $\mu_{eff.}$ correspond to the electronic

TABLE I Analytical and magnetochemical data of the complexes *7–8*, obtained by the methods A and B

					Contents of nitrogen, %				
No.	*R*	*M*	*m.p., °C*	*Brutto-formula*	*Found (A)*	*Found (B)*	*Calcd.*	$\mu_{eff.}$, *A*	*B.M. B*
1	H	Cu	245–247	$C_{30}H_{20}N_2O_8S_2Cu$	4.10	4.18	4.22	1.85	1.88
2	H	Ni	> 250	$C_{30}H_{20}N_2O_8S_2Ni$	4.30	4.28	4.25	3.08	3.15
3	H	Co	248	$C_{30}H_{20}N_2O_8S_2Co$	4.18	4.23	4.25	4.91	–
4	H	Zn	223–225	$C_{30}H_{20}N_2O_8S_2Zn$	4.10	4.18	4.21	Dia	Dia
5	CH_3	Cu	> 250	$C_{32}H_{24}N_2O_8S_2Cu$	4.00	4.08	4.05	1.91	–
6	CH_3	Ni	250	$C_{32}H_{24}N_2O_8S_2Ni$	3.97	4.01	4.08	3.25	–
7	CH_3	Co	250	$C_{32}H_{24}N_2O_8S_2Co$	3.96	3.93	4.08	4.78	–
8	CH_3	Zn	250	$C_{32}H_{24}N_2O_8S_2Zn$	3.97	3.95	4.04	Dia	–

configurations $[Ar]3d^{10}$, $[Ar]3d^9$, $[Ar]3d^8$, $[Ar]3d^7$ for divalent zinc, copper, nickel, and cobalt ions, respectively. The magnitudes of magnetic moments testify directly that the coordination sphere of all the complexes are not planar and can be ascribed to tetrahedral or octahedral structures [11–13].

The studies above show the synthesized complexes have the β-diketonate chelate structure *7–8*, which, in a difference of *4* or *9*, contains the coordination knot MO_4.

CONCLUSIONS

The novel chelates ML_2 (M = Co, Ni, Cu, Zn) were obtained by interaction of 3-benzoyl-4-hydroxy-1,2-benzothiazine-4(3H)-on-1,1-dioxide and 2-methyl-3-benzoyl-4-hydroxy-1,2-benzothiazine-4(3H)-on-1,1-dioxide (LH) with elemental metals (direct electrochemical synthesis) or their acetates (chemical synthesis) in methanol. The complexes, prepared by different methods above, have the same composition ML_2, IR- and NMR-spectral, and magnetochemical characteristics and can be used as model compounds to develop anti-inflammatory drugs. Spectrochemical studies show the synthesized complexes have the β-diketonate chelate structures *7–8* with coordination MO_4.

Acknowledgement

The authors are grateful to the financial support of the *Universidad Autónoma de Nuevo León* (Monterrey, Mexico) for the financial support of the part of this work (Project PAICyT CA362-00).

References

[1] D. O. Harrison, R. Thomas, A. E. Underhill, J. K. Fletcher, P. S. Gomm and F. Hallway, *Polyhedron* **4**(4), 681 (1985).

[2] R. Cini, G. Giorgi, A. Cinquantini, C. Rossi and M. Sabat, *Inorg. Chem.* **29**(26), 5107 (1990).

[3] M. A. Méndez-Rojas, F. Cordova-Lozano, G. Gójon-Zorrilla, E. González-Vergara and M. A. Quiroz, *Polyhedron* **18**, 2651 (1999).

[4] M. D. Mashkovskii, *Medicines of XX Century*. Moscow: Novaya Volna. p. 154 (1998).

[5] A. von Zelewsky, *Stereochemistry of Coordination Compounds*. Chichester-New York: J. Wiley, 1996, 254 pp.

[6] A. D. Garnovskii, D. A. Garnovskii, I. S. Vasilchenko, A. S. Burlov, A. P. Sadimenko and I. D. Sadekov, *Russ. Chem. Rev.* **66**(5), 389 (1997).

[7] K. Abe, S. Yamamoto and K. Matsui, *J. Pharm. Soc. Japan* **76**, 1058 (1956); *Chem. Abstr.* **51**, 3499 (1957).

[8] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*. London: Methuen; New York: J. Wiley, 1961.

[9] L. J. Bellamy, *Advances in Infrared Group Frequencies*. Methuen and Co. Ltd. Bungay, Suffolk, 1968.

[10] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Brisbane-Toronto-Singapore: J. Wiley, 1986, 3rd; New York, 1997, 5th.

[11] R. C. Mehrotra, R. Rohra and D. P. Gran, *Metal-Diketonates and Allied Derivatives*. New York: Acad. Press, 1978.

[12] L. M. Shkolnikova and M. A. Porai-Koshitz, *Results of Science and Technology. Crystallochemistry*. Moscow: VINITI. **15**, 117 (1982).

[13] A. R. Siedle, *Comprehensive Coordination Chemistry*. (G. Wilkinson, Ed.). Oxford: Pergamon Press **2**, 365 (1987).