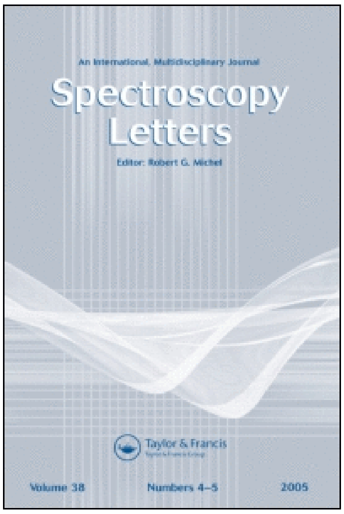


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

SPECTRAL AND MAGNETIC STUDIES OF THE Co(II), Ni(II), Zn(II), AND Cd(II) COMPLEXES WITH 1H-1,2,4-TRIAZOLE-3-THIOL AND 3-AMINO-5-MERCAPTO-1,2,4-TRIAZOLE

M. Gabryszewski[a]
[a] Institute of Chemistry, Pedagogical University, Kielce, Poland

To cite this Article Gabryszewski, M.(2001) 'SPECTRAL AND MAGNETIC STUDIES OF THE Co(II), Ni(II), Zn(II), AND Cd(II) COMPLEXES WITH 1H-1,2,4-TRIAZOLE-3-THIOL AND 3-AMINO-5-MERCAPTO-1,2,4-TRIAZOLE', Spectroscopy Letters, 34: 1, 57 — 63

To link to this Article: DOI: 10.1081/SL-100001451

URL: http://dx.doi.org/10.1081/SL-100001451

SPECTROSCOPY LETTERS, 34(1), 57–63 (2001)

SPECTRAL AND MAGNETIC STUDIES OF THE Co(II), Ni(II), Zn(II), AND Cd(II) COMPLEXES WITH 1H-1,2,4-TRIAZOLE-3-THIOL AND 3-AMINO-5-MERCAPTO-1,2,4-TRIAZOLE

M. Gabryszewski

Institute of Chemistry, Pedagogical University,
25020 Kielce, Poland

ABSTRACT

The complexes of 1H-1,2,4-triazole-3-thiol and 3-amino-5-mercapto-1,2,4-triazole with Co(II), Ni(II), Zn(II), and Cd(II) were prepared and characterized on the basis of chemical analyses, infrared and visible spectroscopy, and magnetic susceptibility data. The polymeric nature of the complexes was established. The anionic ligands were coordinated through the ring nitrogen atom and the egzocyclic sulphur atom.

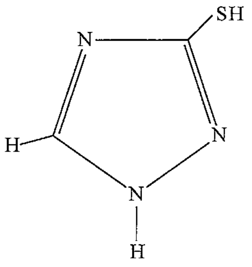
Key Words: IR spectroscopy; *far*-IR spectroscopy; Electronic visible spectra; Magnetic measurements

INTRODUCTION

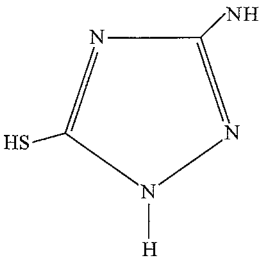
1H-1,2,4-Triazole-3-thiol (**I**) and 3-amino-5-mercapto-1,2,4-triazole (**II**) are interesting ligands as they have at least two donor centers available for coordination.

The coordination compounds of 1H-1,2,4-triazole-3-thiol and 3-amino-5-mercapto-1,2,4-triazole with Co(II) and Ni(II) were previously investigated in aqueous solution by means of the pH-metric method and absorption spectra (1). The ligands were coordinated as anions after dissociation of the proton from the thiol group. The coordination number six, characteristic for aquo-complexes of those cations, was retained in the complexes. The solid Ag(I) complexes of these two ligands were prepared and characterized on the basis of elemental analyses and infrared spectra (2). The ligand:metal ratio equals 1:1 for these complexes. It has been found that the ligands form polymeric complexes with Ag(I), where the endocyclic nitrogen atom and egzocyclic sulphur atom create coordination bonds.

In the present paper, I report syntheses and properties of the complexes of Co(II), Ni(II), Zn(II), and Cd(II) with 1H-1,2,4-triazole-3-thiol and 3-amino-5-mercapto-1,2,4-triazole. The studies were made with the use of elemental analyses, IR and *far*-IR spectroscopy, visible reflectance spectra, and room temperature magnetic susceptibility measurements.



I



II

EXPERIMENTAL

Preparation of Complexes

1H-1,2,4-Triazole-3-thiol (Aldrich), m.p. 221–224°C, and 3-amino-5-mercapto-1,2,4-triazole (Aldrich), m.p. 138–139°C, were used without further purification. Abbreviations TSH and ATSH will be used for the ligands, respectively. Thus, the anions will be abbreviated as TS^- and ATS^-, respectively. Other chemicals were purchased from POCh-Gliwice (Poland).

The metal complexes were prepared according to the general procedure described in the following text. A warm solution of 8 mmol of ligand in 50 cm^3 of a mixture of ethanol and water (1:1) neutralized with NH_4OH was added to a warm solution of 4 mmol of metal chloride in the same solvent. The complexes precipitated slowly. They were digested on a water-bath for several hours; washed repeatedly with warm water, ethanol, and ethyl ether; and dried in a vacuum desiccator. It was impossible to obtain single crystals available for X-ray investigations.

Physical Measurements

Elemental analyses of the complexes were carried out using the Perkin-Elmer Model 240 Analyzer. The IR spectra in the range 4000–400 cm^{-1} were obtained with the use of KBr pellets on a Specord M80 spectrophotometer (Zeiss, Jena). The *far*-IR spectra in the range 400–100 cm^{-1} were obtained with the application suspensions of the compounds in acetone into a polyethylene window on a DigiLab FTS-60 spectrophotometer. The reflectance spectra in visible range were obtained with the use of Li_2CO_3 pellets on a Hitachi 365 UV–vis spectrophotometer. The resolution processing of the weakly resolved bands was performed with the use of the computer program Origin 5.0 from Microcal Software, Inc. The multipeaks analysis with the Gaussian equation was used for this purpose. The magnetic susceptibility measurements at room temperature were made on a Magnetic Susceptibility Balance from Sherwood Scientific. The effective magnetic moments were calculated from the equation $\mu = 2.83\sqrt{\chi T}$ (B.M.), where χ is the molar susceptibility of sample. The distribution of charge density for anionic ligands was calculated by PM3 semiempirical method, with the use of the computer program Hyper Chem 5.01 from Hypercube, Inc.

RESULTS AND DISCUSSION

The analytical results of all the complexes are in good agreement with the suggested stoichiometries (Tab. 1). Calculations were made with the assumption

Table 1. Analytical Data[a] of the TSH and ATSH Complexes

Complex	C(%)	H(%)	N(%)	S(%)
$Co(TS)_2(H_2O)_2$	16.21 (16.27)	2.69 (2.73)	28.12 (28.47)	21.98 (21.72)
$Ni(TS)_2(H_2O)_2$	16.34 (16.29)	2.70 (2.73)	28.03 (28.49)	21.93 (21.74)
$Zn(TS)_2(H_2O)_2$	16.21 (15.93)	2.71 (2.67)	27.47 (27.86)	21.45 (21.26)
$Cd(TS)_2(H_2O)_2$	13.94 (13.78)	2.38 (2.31)	23.86 (24.10)	18.34 (18.39)
$Co(ATS)_2(H_2O)_2$	14.56 (14.77)	3.16 (3.10)	34.24 (34.45)	19.34 (19.72)
$Ni(ATS)_2(H_2O)_2$	14.71 (14.78)	3.04 (3.10)	34.18 (34.48)	19.93 (19.73)
$Zn(ATS)_2$	16.45 (16.25)	2.17 (2.04)	37.98 (37.90)	21.92 (21.69)
$Cd(ATS)_2$	13.91 (14.02)	1.58 (1.76)	32.31 (32.70)	18.47 (18.71)

[a] Calculated values are given in parentheses.

that the —SH group undergoes ionization. All the complexes include deprotonated anionic ligands. The ligand:metal ratio equals 2:1 in all the complexes. All the complexes are insoluble in usual organic solvents and appear to be polymeric in nature.

The positions and proposed assignments of major infrared bands in the spectra of the ligands and their complexes are shown in Table 2. The ν(OH), $\nu(NH_2)$, ν(NH), and ν(CH) stretching vibrations are observed in the spectra of the appropriate complexes (3). Sometimes only one strong broad band is visible at 3100–3550 cm^{-1}, which consists of these vibrations. The absence of S—H stretching frequency (3–5) at 2617 cm^{-1} in the spectra of the complexes confirms the analytical results that the ligands are in deprotonated forms, which suggests sulphur coordination. The complexation effect is also pronounced via C═N vibrations. The strong or medium absorption bands occur in the range 1360–1558 cm^{-1}. These absorptions involve ν(C—N) stretching vibrations. The bands in the spectra of the complexes are shifted to lower frequencies as a result of the bond formation between the nitrogen atom of the heterocyclic ring and the metal cation (4,6). The presence of water molecules within the coordination sphere is supported by the presence of bands at ca. 3500 and 1610 cm^{-1} assigned to ν(OH) and δ(HOH), respectively (7).

A comparison of the *far*-IR spectra of the ligands and the complexes reveals that the new bands, not present in the ligands, appear in the complexes. In the spectra of all the complexes, bands occur in the range 225–256 cm^{-1}. These bands can be attributed to the M—N stretching vibrations (7), which suggests coordination through the nitrogen atom. The bands in the range 324–378 cm^{-1} can be assigned to the M—S stretching vibrations (7). In the spectra of complexes that contain water molecules, the bands in the range 431–496 cm^{-1} can be observed. These bands are presumably due to the M—O stretching vibrations (6). The bands in the *far*-IR spectra suggest that TSH and ATSH act as bidentate ligands coordinating through the nitrogen atom and the egzocyclic sulphur atom. The polymeric nature of Ag(I) complexes with these ligands has been reported previously (2).

The reflectance bands of electronic spectra and the room temperature magnetic moments of the Co(II) and Ni(II) complexes are listed in Table 3. The bands of electronic spectra correspond to the d–d electron transitions in the ligand field with octahedral symmetry (8,9). In the spectra of black Co(II) complexes there are strong charge transfer bands above 29,000 cm^{-1}. The room temperature magnetic moments of complexes lie in the ranges that are characteristic of high spin Co(II) and Ni(II) complexes in octahedral environment (9).

The calculations of the charge density distributions for the anionic ligands show that the highest negative charge is located on the nitrogen atom at position 2 of the heterocyclic ring. It is presumably the second coordination center of the ligands. It is worth stressing that all the 1,2,4-triazoles are tautomeric

Table 2. Important Infrared Absorption Bands[a] in the Spectra of TSH and ATSH and Their Complexes

Compound	ν(OH)	$\nu(NH_2)$	ν(NH)	ν(CH)	ν(SH)	$\delta(H_2O)$	$\delta(NH_2)$	ν(C=N)	Other Bands
TSH			3083s	2958s	2617w			1558s 1475s	
$Co(TS)_2(H_2O)_2$	Strong broad band at 3100–3550					1624mbr		1476mbr 1360m	225m (Co–N) 334mbr (Co–S) 430mbr (Co–O)
$Ni(TS)_2(H_2O)_2$	Strong band at ca. 3400 with shoulder at ca. 3200					1616mbr		1472mbr 1360m	252s (Ni–N) 336s (Ni–S) 431s (Ni–O)
$Zn(TS)_2(H_2O)_2$	3200–3550sbr		3115s	2965m		1616sbr		1490s 1375sbr	250w (Zn–N) 328m (Zn–S) 471mbr (Zn–O)
$Cd(TS)_2(H_2O)_2$	3200–3550sbr		3115s	2965m		1616mbr		1476s 1370s	252s (Cd–N) 324m (Cd–S) 432s (Cd–O)
ATSH		3379s 3267s	3105s		2617w		1652s	1546s 1473s	
$Co(ATS)_2(H_2O)_2$	Strong broad band at 3100–3550					1605s	1630s	1516s 1464s	238mbr (Co–N) 376m (Co–S) 491sbr (Co–O)
$Ni(ATS)_2(H_2O)_2$	Strong broad band at 3100–3550					1600s	1628s	1500m 1460w	256mbr (Ni–N) 377m (Ni–S) 496sbr (Ni–O)
$Zn(ATS)_2$		3432s 3358s	3200s				1624s	1540s 1432s	251s (Zn–N) 376s (Zn–S)
$Cd(ATS)_2$		3456s 3352s	3215w				1648s	1556m 1488m	226s (Cd–N) 378m (Cd–S)

[a] s–strong, m–medium, w–weak, br–broad, sh–shoulder.

Table 3. Electronic Reflectance Bands (cm^{-1}) and Room Temperature Magnetic Moments (B.M.) of TSH and ATSH Complexes

Complex	Electronic Bands and Their Assignments		μ_{eff}
$Co(TS)_2(H_2O)_2$	16942	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.62
	29380	Charge transfer	
$Ni(TS)_2(H_2O)_2$	15862	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	3.16
	24736	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Co(ATS)_2(H_2O)_2$	17244	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.73
	29550	Charge transfer	
$Ni(ATS)_2(H_2O)_2$	15438	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	3.14
	24224	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	

and the position of the proton is variable. Thus, an endocyclic nitrogen atom taking part in the coordination to a metal cation may be any nitrogen of the ring.

ACKNOWLEDGMENT

The author wishes to thank Mrs. B. Wieczorek for the syntheses of complexes.

REFERENCES

1. Gabryszewski, M. The Stability of 1H-1,2,4-Triazole-3-thiol and 3-Amino-1,2,4-triazole Complexes of Co(II) and Ni(II) in Aqueous Solution. Polish J. Chem. **1994**, *68*, 1895–97.
2. Gabryszewski, M. Silver (I) Complexes of 1H-1,2,4-Triazole-3-thiol, 3-Amino-5-mercapto-1,2,4-triazole and 3-Amino-5-methylthio-1,2,4-triazole. Polish J. Chem. **1996**, *70*, 1220–22.
3. Silverstein, R.M.; Bassler, G.C.; Morill, T.C. *Spectrometric Identification of Organic Compounds*; New York: Wiley, 1991.
4. Zaidi, S.A.A.; Varshney, D.K. The Nature of the Complexes of 2,5-Dimercato-1,3,4-tiadiazole (Bismuthiol) with Copper(I) and Copper(II). J. Inorg. Nucl. Chem. **1975**, *37*, 1804–806.
5. Zaidi, S.A.A.; Varshney, D.K.; Siddiqi, K.S.; Siddiqi, Z.A.; Islam, V. Bismuthiol I Complexes of Fe(II), Fe(II), Ru(I), Pd(II), Pt(IV), Ag(I), Au(I), Ir(VI) and Tl(III). Acta Chim. Acad. Sci. Hung. **1977**, *95*, 383–88.

6. Czakis-Sulikowska, D.; Radwanska-Doczekalska, J.; Kuznik, B.; Malinowska, A. 2,4′−Bipyridyl Complexes with Silver(I) and Copper(II). Transition Met. Chem. **1996**, *21*, 19–22.
7. Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Chemistry*; New York: Wiley, 1978.
8. Lever, A.B.P. *Inorganic Electronic Spectroscopy*; Amsterdam: Elsevier, 1980.
9. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*; New York: Wiley, 1970.

Received November 30, 1999
Accepted July 20, 2000

Downloaded At: 03:13 30 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SL100001451