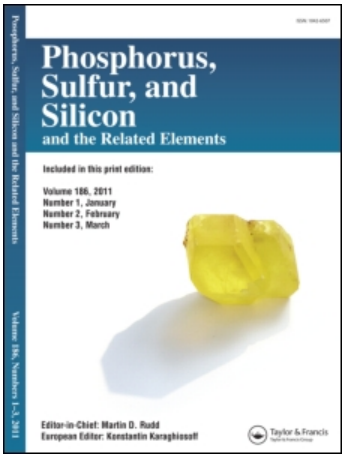


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

COMPLEXING ABILITY OF SOME 2-PYRAZOLINE- 4-DITHIOCARBOXYLIC ACID DERIVATIVES

S. A. El-gyar[a]; M. A. El-gahami[a]; M. M. Kandeel[a]
[a] Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

To cite this Article El-gyar, S. A. , El-gahami, M. A. and Kandeel, M. M.(1991) 'COMPLEXING ABILITY OF SOME 2-PYRAZOLINE- 4-DITHIOCARBOXYLIC ACID DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 62: 1, 119 — 125
To link to this Article: DOI: 10.1080/10426509108034467
URL: http://dx.doi.org/10.1080/10426509108034467

Phosphorus, Sulfur, and Silicon, 1991, Vol. 62, pp. 119–125
Reprints available directly from the publisher
Photocopying permitted by license only

COMPLEXING ABILITY OF SOME 2-PYRAZOLINE-4-DITHIOCARBOXYLIC ACID DERIVATIVES*

S. A. EL-GYAR, M. A. EL-GAHAMI and M. M. KANDEEL
Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

(Received March 3, 1991; in final form April 18, 1991)

Substituted 2-pyrazoline-4-dithiocarboxylic acid complexes with Cu(II), Ni(II), Co(II), La(III), Ce(III), Th(IV) and UO_2(II) have been isolated. The structures of the complexes are recognized by elemental analyses, thermal decomposition, electronic and IR spectral data as well as conductance measurements. The ligands are coordinated to the metal ions as monovalent bidentate ligand. Thermogravimetric studies indicate that these complexes are stable up to 180°C and undergo complete decomposition in the range 180–430°C resulting in the formation of stable metal oxides. In Th(IV), Ce(III), or La(III) nitrate complexes, nitrate ions are bidentately coordinated to the metal ion, resulting in the formation of six-coordinate nitrato complexes. The formula of the complexes suggests that, uranyl ion has a coordination number of six. This is achieved by coordination of two molecules of the bidentate title ligands in addition to the two water molecules which have already been bonded to the UO_2(II) species. A distorted octahedral structure is proposed for Cu(II), Ni(II) and Co(II) complexes.

Key words: Metal complexes of 2-pyrazoline-4-dithiocarboxylic acids; electronic and IR spectra; conductance; thermogravic analysis

INTRODUCTION

Generally, substituted pyrazoles have long been acclaimed for their medicinal values. Due to the biological implications of the pyrazole derivatives even in the light against cancer,[1] the coordination chemistry of pyrazole-derived ligands has been taken up only in recent years.[2–5]

Our interest in the coordination chemistry of biologically active compounds led us to study the ligating properties of some-2-pyrazoline-4-dithiocarboxylic acids whose coordination chemistry is less developed in the literature. These compounds were found to have a wide application as drugs and pharmaceutical preparations.[6] We report herein the preparation and characterization of Cu(II), Ni(II), Co(II), La(III), Ce(III), Th(IV) and UO_2(II) complexes of these compounds either in their solid or solution states.

RESULTS AND DISCUSSION

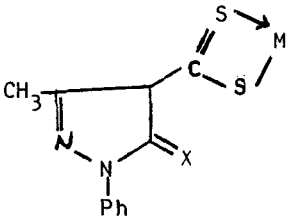
Colors, analytical results and molar conductivity values for the prepared complexes are given in Table I. Two of the ligands used in this study (L_1 and L_2), are flexidentate where they can act as monobasic bidentate (structures I or II) ligands. However, IR and electronic spectra provide ample evidence in favor of the coordination of the ligands through structure II and monobasic bidentate mode as it is given hereafter.

* Presented at the 3rd IBN SINA Symposium Jan. 28–31 (1991), Aswan, Egypt.

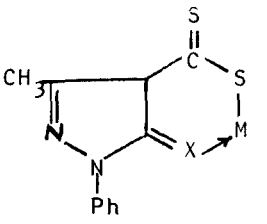
TABLE I

Analytical data, color, decomposition temperature and molar conductance values of the metal complexes

Compound	Decomp. Temp.°C	Colour	Calc.(Found) %				Λ_m
			C	H	N	S	$Ohm^{-1}\ cm^2\ mol^{-1}$(DMF)
Complexes (L_1)							
$[Cu(C_{11}H_{10}N_3S_2)_2 2H_2O]$	305	deep green	44.31 (44.50)	4.05 (4.10)	14.09 (13.80)	21.50 (21.80)	11.33
$[Ni(C_{11}H_{10}N_3S_2)_2 2H_2O]$	310	green	44.68 (44.30)	4.09 (4.30)	14.20 (14.50)	21.68 (21.30)	11.00
$[Co(C_{11}H_{10}N_3S_2)_2 2H_2O]$	280	brown	44.67 (44.90)	4.09 (4.10)	14.20 (13.90)	21.68 (21.80)	4.40
$[La(C_{11}H_{10}N_3S_2)_2 NO_3]$	> 350	yellow	37.87 (38.10)	2.88 (3.10)	14.05 (14.30)	18.38 (18.10)	13.60
$[Ce(C_{11}H_{10}N_3S_2)_2 NO_3]$	> 350	orange	37.81 (37.60)	2.88 (3.00)	14.03 (13.80)	18.35 (18.50)	16.01
$[Th(C_{11}H_{10}N_3S_2)_2 NO_3]NO_3$	340	yellow	30.98 (31.20)	2.36 (2.50)	16.42 (16.70)	15.03 (14.80)	70.60
$[UO_2(C_{11}H_{10}N_3S_2)_2 2H_2O]$	325	pale yellow	32.83 (33.10)	3.00 (3.30)	10.46 (10.50)	15.97 (16.20)	14.60
Complexes (L_2)							
$[Cu(C_{11}H_9N_2S_2O)_2 2H_2O]$	300	brown	44.17 (43.80)	3.70 (4.00)	9.36 (9.20)	21.43 (21.50)	9.30
$[Ni(C_{11}H_9N_2S_2O)_2 2H_2O]$	310	deep green	44.53 (44.80)	3.73 (3.60)	9.44 (9.70)	21.61 (21.90)	11.50
$[Co(C_{11}H_9N_2S_2O)_2 2H_2O]$	330	greenish yellow	44.51 (44.40)	3.73 (3.90)	9.43 (9.20)	21.60 (21.50)	9.01
$[La(C_{11}H_9N_2S_2O)_2 NO_3]$	335	brown	37.77 (38.00)	2.95 (3.20)	10.01 (9.70)	18.33 (18.20)	18.70
$[Ce(C_{11}H_9N_2S_2O)_2 NO_3]$	340	yellow	37.70 (37.50)	2.58 (2.80)	9.99 (10.20)	18.29 (18.50)	16.70
$[Th(C_{11}H_9N_2S_2O)_2 NO_3]NO_3$	> 350	yellow	30.91 (31.20)	2.12 (2.40)	9.83 (10.00)	15.00 (14.80)	85.60
$[UO_2(C_{11}H_9N_2S_2O)_2 2H_2O]$	345	deep yellow	32.83 (33.00)	2.75 (3.00)	6.96 (6.60)	15.93 (16.30)	25.70



I
X = NH, 1-phenyl-3-methyl-5-imino-2-pyrazoline-4-dithiocarboxylic acid (L_1).



II
X = 0, 1-phenyl-3-methyl-2-pyrazolin-5-one-4-dithiocarboxylic acid (L_2).

The results of elemental analysis are consistent with 1:2 metal ion to ligand complexes having the formulae $[M(L)_2X_1\, nH_2O]X_2$, where M = Cu(II), Ni(II), Co(II), UO_2(II); X_1 = 0; n = 2; X_2 = 0; when M = Ce(III) or La(III); $X_1 = NO_3^-$; n = 2; $X_2 = NO_3^-$; when M = Th(IV); $X_1 = NO_3^-$; n = 2; $X_2 = NO_3^-$.

Except in the case of the Th(IV)-complexes, the measured molar conductance values of the other complexes are in the range 4.40 to 25.70 $Ohm^{-1}\ cm^2\ mol^{-1}$. This suggests the nonelectrolyte nature of such complexes.

On the other hand the measured molar conductance values of the Th(IV)-L_1 and L_2 complexes are 70.6 and 85.6 $Ohm^{-1}\ cm^2\ mol^{-1}$ respectively. These values indicate that such complexes are 1:1 electrolytes.[7]

INFRARED SPECTRA

The important IR spectral bands of the free ligands and the complexes are reported in Table II. It is evident from this table that the IR spectra of the metal complexes exhibit marked differences from those of the free ligands.

The spectra of the ligand (L_2) has a strong band at 1640 cm^{-1} which is attributed to the stretching vibration of the ring carbonyl group (C=O). This band acquires an appreciable shift towards lower frequency in the IR spectra of the complexes with the appearance of a new bands at 415–435 cm^{-1} due to (M-O).[8] These shifts (about 10–35 cm^{-1}) in the carbonyl vibrations indicate that the L_2 is coordinated to the metal ion through the carbonyl oxygen.

The absence of S-H stretching frequency band around 2515 and 2510 cm^{-1} in the spectrum of the free L_1 and L_2 respectively, excludes the possibility of the existence of its "Thiol" form at least in the solid state. This is further supported by a new band appearing in the region 650–675 cm^{-1} due to (M-S).[9] This reveals that in all cases, coordination takes place through a proton elimination.

The band observed at 3060 cm^{-1} in the free L_1 ligand due to νNH[10] is found at higher frequencies in the spectra of the corresponding metal complexes. This indicates coordination of the NH group of L_1 to the metal ions,[11] a behaviour which confirms where in new bands are observed around 450–470 cm^{-1} which can be assigned to ν(M-N) vibration.[12]

The two strong bands appearing at 1295 and 1290 cm^{-1} in the IR spectrum of L_1 and L_2 respectively, are assignable to $\nu C{=}S$. There two bands were found to locate, in the IR spectra of the different complexes, at almost the same frequencies

TABLE II

Selected IR bands cm^{-1} for the free ligands and metal complexes

Compound	Assignment						
	ν_{OH}	ν_{NH}	δ_{NH}	$\nu_{C=O}$	$\nu_{(M-N)}$	$\nu_{(M-O)}$	$\nu_{(M-S)}$
Free (L_1)	-	3060	1710	-	-	-	-
Cu(II)-L_1	3460	3090	1750	-	455	-	675
Ni(II)-L_1	3360	3070	1745	-	465	-	660
Co(II)-L_1	3400	3080	1733	-	450	-	650
La(III)-L_1	-	3160	1750	-	450	-	675
Ce(III)-L_1	-	3120	1730	-	470	-	665
Th(IV)-L_1	-	3140	1730	-	460	-	670
UO_2(II)-L_1	3400	3100	1740	-	460	-	675
Free (L_2)	-	-		1640	-	-	-
Cu(II)-L_2	3380	-	-	1625	-	415	670
Ni(II)-L_2	3400	-	-	1630	-	425	670
Co(II)-L_2	3400	-	-	1630	-	435	665
La(III)-L_2	-	-	-	1605	-	430	655
Ce(III)-L_2	-	-	-	1615	-	435	675
Th(IV)-L_2	-	-	-	1610	-	425	650
UO_2(II)-L_2	3390	-	-	1610	-	430	660

as in the spectra of the free ligands. This indicates that the C=S group does not participate in complex formation. This is in confirmation of the conclusion that the complexes are formed through coordination of the sulfur thio atom, and NH group in case of L_1 and the sulfur thio atom and oxygen carbonyl group in case of L_2. Bands due to M-O and M-N stretches are obtained by careful comparison with the IR spectra of the free ligands. With the coordination via the C=S moiety ruled out as described above, appearance of these two bands considered as strong evidence for attachment of the ligands to metal ions according to structure II.

In the IR spectra of the La(III), Ce(III) and Th(IV) complexes three additional bands which are not present in the spectra of the free ligands are observed. These three bands appear at 1460–1490, 1280 and 1020 cm^{-1}. These three bands are assigned respectively to ν_4, ν_1 and ν_2 mode of the nitrate ion. Since the magnitude of splitting of $\nu_4 - \nu_1$ is 180–210 cm^{-1} in the metal nitrate complexes, therefore nitrate ions are coordinated to La(III), Ce(III) or Th(IV) ions in a bidentate fashion.[13] The conductivity data (cf. Table I) confirms coordination of one nitrate group in each complex of these metal ions.

The IR bands due to UO_2^{2+} group are observed near 890 and 800 cm^{-1} as strong and weak bands corresponding to the asymmetric stretching frequency $\nu_3(UO_2)$ and the symmetric stretching frequency $\nu_1(UO_2)$ respectively. These observations indicate that the UO_2^{2+} moiety in the present compounds is virtually linear.[14]

The presence of coordinated water molecules in the prepared UO_2(II), Cu(II), Ni(II) or Co(II) chelates has been confirmed by the new band appeared at 3460–3380 cm^{-1} in the IR spectra of the complexes. Also, the rocking mode of coordinated water appeared as a weak vibration band in the neighbourhood of 910–950 cm^{-1}.[15]

ELECTRONIC SPECTRA

The electronic spectra of DMF solution of the complexes are recorded in the wavelength range 300–800 nm, ν_{max} and ε_{max} values of the different absorption bands are recorded in Table III. The first band that appeared with ν_{max} in the range 27,700–35,300 cm^{-1} is due to intraligand electronic transition.[16] The bands having ν_{max} in the range 20,000–24,700 cm^{-1} are attributable to an LMCT transition.

The third band appearing in the absorption spectra of Co(II) complexes was found to ν_{max} at 17,300 cm^{-1}. This band is due to a d-d electronic transition within the Co(II) chelates and lies in the range reported for six coordinate Co(II) complexes.[17] The position of this band is suggestive for a distorted octahedral geometry around Co(II), ion. Therefore, this band can be assigned to the transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. Ni(II) complexes solutions comprise a band at 16,900 cm^{-1} indicative of octahedral Ni(II) complexes and this band is believed to be due to $^3A_2(F) \rightarrow {}^3T(F)$.

The bands appearing at 19,500 cm^{-1} in the case of Cu(II) complexes are assigned to $^2E_{2g} \rightarrow {}^2T_{2g}$, which are usually found for tetragonal Cu(II) complexes.[17]

It is noteworthy that the considerably high molar absorptivity of the d-d bands of both Co(II), Ni(II), and Cu(II) chelates suggests a distorted octahedral geometry of the synthesized chelates.[17]

TABLE III

Electronic spectra of the metal chelats

Compound	$\nu_{max}(cm^{-1}).(\varepsilon_{max}\ mol^{-1}\ cm^{2})$
Co(II)-L_1	17,300(242); 30,300(4027)
Ni(II)-L_1	16,900(180); 29,800(6398); 33,300(3365).
Cu(II)-L_1	19,500(71); 27,700(3214); 35,300(6788).
La(III)-L_1	22,700(2500); 31,500(3929).
Ce(III)-L_1	24,400(2387); 27,800(5032); 32,800(5935).
Th(IV)-L_1	20,000(3675); 33,300(2838).
UO_2(II)-L_1	22,300(593); 32,300(4593).
Co(II)-L_2	17,000(175); 30,300(1810).
Ni(II)-L_2	16,900(200); 25,600(3750); 29,400(7250).
Cu(II)-L_2	19,500(210); 30,300(4670); 33,600(8920).
La(III)-L_2	22,700(214); 30,300(3571).
Ce(III)-L_2	23,500(1345); 27,800(2836); 31,700(3345).
Th(IV)-L_2	21,700(630); 29,400(3520); 32,300(3800).
UO_2(II)-L_2	21,600(607); 28,600(2033).

THERMOGRAVIMETRIC ANALYSIS

TGA technique have been used to follow the thermal behaviour of these complexes. According to the results obtained, the complexes are not volatile and their decomposition takes place in different steps. In the Cu(II), Co(II), Ni(II) and UO_2(II) complexes a definite loss in mass occurs between 180–210°C corresponds to the presence of the coordinated two water molecules. This step is followed by the loss of the ligand molecules in the temperature range 250–430°C, giving the corresponding metal oxide.

EXPERIMENTAL

Preparation of the organic ligands and metal complexes: The-2-pyrazoline-4-dithiocarboxylic acid derivatives were prepared and characterized as described by Matolesy et al.[18]

The metal complexes were prepared according to the following method. An aqueous alc. solution of hydrated Cu(II), Co(II) or Ni(II) chloride; La(III), Ce(III) or Th(IV) nitrate; UO_2(II) acetate (0.01 mol) was added to an ethanolic solution of the corresponding ligand (0.025 mol).

The reaction mixture was stirred under reflux on a water-bath for 20–50 min and cooled to room temperature. The solid products were filtered off, washed several times with diethylether and dried under vacuum over P_4O_{10}.

Physical Measurements. UV-visible spectra were recorded on a CECIL 599 spectrophotometer using 1 cm matched silica cells. IR spectra were obtained as KBr disks using a Perkin-Elmer 599-B spectrophotometer. Conductivity measurements were carried out using a Pyebridge in DMF solutions at 0.001 M concentration. All measurements were carried out at room temperature (~25°C).

REFERENCES

1. G. Sobhanadevi and P. Indrasenan, *Inorg. Chim. Acta,* **133,** 157 (1987).
2. J. Chacko, *Synth. React. Inorg. Met-Org. Chem.,* **12,** 361 (1982).
3. V. Giri and P. Indrasenan, *Polyhedron,* **2,** 573 (1983).
4. A. N. Cost and I. I. Grandberg, "In Advances in Heterocyclic Chemistry" Vol. 6, p. 384, Academic Press, New York 1966.
5. Babu Kuncheria and P. Indrasenan, *Polyhedron,* **7,** 143 (1988).
6. D. R. Williams, *Chem. Rev.,* **72,** 203 (1972).
7. W. J. Geary, *Coord. Chem. Rev.,* **7,** 81 (1971).
8. S. K. Sengupta, S. K. Sahni and R. N. Kapoor, *Polyhedron,* **2,** 317 (1983).
9. K. K. Aravindakshan and C. G. R. Nair, *Indian J. Chem.,* **20A,** 684 (1981).
10. J. K. Kovacic, *Spectrochim. Acta,* **23A,** 183 (1967).
11. B. Prabhakar and P. Lingainah, *Polyhedron,* **9,** 805 (1990).
12. J. R. Ferraro, "Low-Frequency Vibrations of Inorganic and Coordination Compounds," Plenum, New York, 1971.
13. N. F. Curtis and Y. M. Curtis, *Inorg. Chem.,* **4,** 804 (1965).
14. H. A. Tajmir-Riahi and A. Sarkheil, *Monatsh. Chem.,* **112,** 1261 (1981).
15. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley, New York, 1963, p. 156.
16. S. A. Ibrahim, M. A. El-Gahami and A. M. Hammam, *Chemica Scripta,* **29,** 229 (1989).
17. A. B. P. Lever "Inorganic Electronic Spectroscopy" Elsevier, Amsterdam 1968.
18. G. Matolesy, P. Sohar and B. Bordas, *Chem. Ber.,* **104,** 115 (1971).