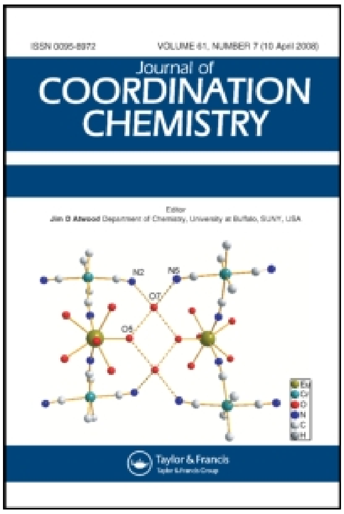

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Mostafa, M. M. and El-asmy, A. A.(1983) 'TRANSITION METAL COMPLEXES OF 1-ISOVALERYL-4-PHENYL-3-THIOSEMICARBAZIDE', Journal of Coordination Chemistry, 12: 3, 197 — 202
To link to this Article: DOI: 10.1080/00958978308073848
URL: http://dx.doi.org/10.1080/00958978308073848

J. Coord. Chem., 1983, Vol. 12, pp. 197-202
0095-8972/83/1203-0197 $18.50/0

TRANSITION METAL COMPLEXES OF 1-ISOVALERYL-4-PHENYL-3-THIOSEMICARBAZIDE

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(Received July 5, 1982)

The complexes of 1-isovaleryl-4-phenyl-3-thiosemicarbazide (IVPTS) with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) have been prepared and characterized on the basis of elemental analyses, molar conductance, magnetic moment and spectral (visible, IR, NMR) studies. Square-planar geometry have been proposed for Ni(II) and Cu(II) and octahedral for the Co(II) complex.

INTRODUCTION

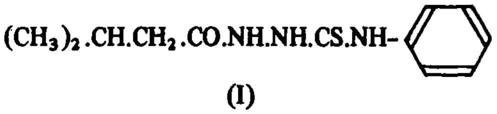
Recently we reported[1-3] an extensive series of complexes derived from thiosemicarbazide derivatives with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) salts. The previous studies revealed that these ligands coordinate via NH and thioenol groups confirmed by conventional physical and chemical measurements. In contrast we found that 1-isovaleryl-4-phenyl-3-thiosemicarbazide behaves in different way in that the ligand coordinates *via* NH and carbonyl oxygens in the enol form and/or to carbonyl oxygens only.

RESULTS AND DISCUSSION

Analytical data are given in Table 1. The complexes $[Hg(IVPTS)Cl_2]$, $[M(IVPTSH)_2].YH_2O$ (M=Ni(II), Cu(II), Cd(II) and Y=5 in case of Cu(II)), $[M(IVPTS)_2Cl_2].YH_2O$ (M=Cu(II), Zn(II) and Y=1 in case of zinc), $[Cu(IVPTS)Br_2(H_2O)].H_2O$, $[Co(IVPTSH)Cl(H_2O)_3]$, $[Cu(IVPTS)_2Py_2Cl_2]$ and $[Ni(IVPTSH)_2Py_2]$ were obtained as indicated in the experimental section. All the complexes are insoluble in common organic solvents, but easily soluble in DMF or DMSO. Their molar conductivities in DMSO are considerably lower than those of uni-univalent electrolytes in this solvent.[4] This indicates that the complexes are predominantly covalent in nature.

Infrared Spectral Studies

The bonding sites have been determined by a careful comparison of the infrared spectra of the solid complexes with those of 1-isovaleryl-4-phenyl-3-thiosemicarbazide (I) and isovaleric acid hydrazide[5] and by comparison with previous work.[1-3]



(I)

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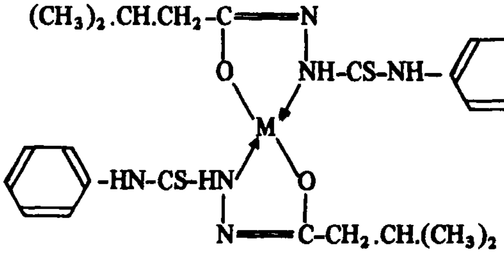
TABLE I
Analytical data and other physical properties

Compound	MP	Colour	% Calculated				% Found				λ_m
			C	H	M	Cl or Br	C	H	M	Cl or Br	in DMSO
IVPTS	136°	white	57.34	6.82			57.84	6.53			
$[Cu(IVPTS)_2Cl_2]$	190°	pale brown	45.24	5.38	9.97	11.13	45.65	5.74	9.92	11.10	13
$[Cu(IVPTS)_2Py_2Cl_2]$	197°	grey	51.34	5.58			51.11	5.39			
$[Cu(IVPTS)Br_2(H_2O)].H_2O$	195°	olive green	28.22	4.14	12.44	31.29	27.92	4.05	12.90	30.80	18
$[Cu(IVPTSH)_2]5H_2O$	235°	violet	43.92	6.54	9.68		43.89	6.80	10.10		14
$[Co(IVPTSH)Cl(H_2O)_3]$	252°	brown	36.14	5.56	8.89	14.78	36.45	4.35	14.00	8.30	18
$[Zn(IVPTS)_2Cl_2].H_2O$	176°	white	43.87	5.52		10.79	43.74	4.98		11.10	17
$[Hg(IVPTS)Cl_2]$	300°	white	27.56	3.28	38.37	13.56	27.59	3.21	38.70	13.00	26
$[Ni(IVPTSH)_2]$	210°	yellow	51.53	5.77	10.49		50.35	5.65	10.30		15
$[Ni(IVPTSH)_2Py_2]$	216°	violet	56.91	5.90	8.18		26.97	6.11	8.01		7
$[Cd(IVPTSH)_2]$	169°	white	47.02	5.26	18.34		46.33	4.88	18.26		12

The carbonyl band at 1700 cm^{-1} in the spectrum of the ligand is absent in the spectra of Co(II), Ni(II), Cu(II) (other than chloride and bromide) and Cd(II), while it shifts to lower wave-numbers in the spectra of Cu(II) chloride, and bromide, Zn(II) and Hg(II) complexes. It has been found earlier,[6] in ligands containing both thioketo and carbonyl oxygen groups, that the enolization takes place through the thioketo more easily than the carbonyl group. In contrast to this, we found that the carbonyl oxygen takes part in bonding either through enolization as in the case of Co(II), Ni(II), Cu(II) and Cd(II) complexes or through simple coordination in, for example, the Cu(II), Zn(II) and Hg(II) complexes. The enolization of the carbonyl group is preformed *via* the adjacent NH group (II).



M = Ni(II), Cu(II), Cd(II)

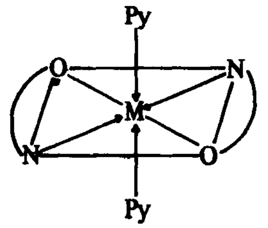
(II)

The proposed structure is supported by the following evidence.

The appearance of new bands attributable to $\nu_{C=N}$, ν_{C-O} and ν_{M-O}[6] at 1620, 1220 and 430 cm^{-1} respectively. The position of the thioketo group bands at 1280 and 740 cm^{-1} in the spectra of all complexes indicates that this group is not taking part in complexation. The band at 980 cm^{-1} due to ν_{N-N} is shifted to higher wave numbers which suggests the involvement of at least one of the NH groups in bonding. The small positive shifts (5-10 cm^{-1}) of this band gives support for participation of one of the NH groups.[7]

On the other hand, the complexes of Cu(II) chloride, bromide, Zn(II) and Hg(II) show a negative shift of the carbonyl group suggesting that the carbonyl oxygen is taking part in coordination. Both the thioketo and the NH groups remain, as evidenced by the spectra of the complexes. This may suggest that the ligand acts as a monodentate.

The isolated pyridine complexes show bands at 3070, 1010, 935 and 820 cm^{-1} due to *C-H* stretching and deformation vibrations. Also, the bands at 1610 and 1515 cm^{-1}, which assigned as coupled modes consisting of $\nu_{C=C}$ and $\nu_{C=N}$, prove the addition of pyridine molecules to the complexes. On the basis of elemental analyses we believe that the pyridine complexes may have structure (III).



M = Ni(II), Cu(II)

(III)

Magnetic and Spectral Studies

Details of the solution spectra of the complexes in DMSO together with values of magnetic moments are listed in Table II. The spectra of the Ni(II) complex shows a band at 20000 cm^{-1} assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in square-planar geometry.[8] The diamagnetic behaviour of the complex lends support for the existence of a square planar Ni(II) ion. The addition of pyridine to the yellow complex [Ni(IVPTSH)$_2$] changes the colour to violet with the appearance of a new band at 17540 cm^{-1} assigned to ν_2 transition in octahedral geometry as found in [Ni(2,5-diMePy)$_2$Br$_2$][9]. This observation can be taken as an evidence for structure (III).

The observed magnetic moment (4.92 B.M.) for the complex [Co(IVPTSH)Cl(H$_2$O)$_3$] and the existence of two bands at 14940 [Co(IVPTSH)Cl(H$_2$O)$_3$] and 17920 cm^{-1} due to $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(F)$ transitions are in a good agreement with those reported for octahedral Co(II) complexes.[10] The fact that the water molecules are not removed when the complex is dried *in vacuo* over phosphorous pentoxide or heated in the oven up to 140° may suggest the presence of water molecules in the coordination sphere. The existence of a broad band centred at 3450 cm^{-1} in the spectrum of the cobalt complex and the lack of this band in the spectrum of the Ni(II) complex can be taken as evidence for the presence of coordinated water in the former. Strong evidence for the presence of coordinated water molecules in the Co(II) complex comes from the proton magnetic resonance spectra of solutions of the diamagnetic complexes in d$_6$-DMSO. In for example, a solution of [Zn(IVPTS)$_2$Cl$_2$].H$_2$O, the –OH proton signal at 12.95 ppm downfield from TMS disappears upon addition of D$_2$O.

The Cu(II) complexes show a broad band in the region 14000-18500 cm^{-1} with a shoulder at ~ 23000 cm^{-1} which lie in the region for those reported for square planar geometry.[11]

EXPERIMENTAL

1-Isovaleryl-4-phenyl-3-thiosemicarbazide was prepared by adding slowly the appropriate volume of phenyl isothicyanate to a solution of isovaleric acid hydrazide in ethanol. The white product was crystallized several times from absolute ethanol. The purity was checked by elemental analysis (MP 136°).

Preparation of the solid complexes

Monoligand complexes were obtained by mixing equimolar amounts of IVPTS and the

TABLE II
Spectral and magnetic properties of IVPTS complexes

Compound	Magnetic moment μ_{eff} (BM)	Electronic Spectra in DMSO (cm^{-1})	
		Ligand field bands	Charge-transfer
[Cu(IVPTS)$_2$Cl$_2$]	1.86	18,450	23,480
[Cu(IVPTS)$_2$Py$_2$Cl$_2$]		14,080	30.300
[Cu(IVPTS)Br$_2$(H$_2$O)].H$_2$O	1.96	14,290	23,300
[Cu(IVPTSH)$_2$].5H$_2$O	1.84	17,540	23,300
[Co(IVPTSH)Cl(H$_2$O)$_3$]	4.92	12,200; 14,840; 16,670; 17,920	
[Ni(IVPTSH)$_2$]	diamagnetic	20,000	34,970
[Ni(IVPTSH)$_2$Py$_2$]		12,990; 17,540	

metal salt in absolute ethanol, whereas the other complexes were obtained when excess ligand was added. The reaction mixture was refluxed on a water bath for 15 minutes. On cooling, the complexes separated as a fine powder. The complexes were filtered off, washed several times with hot ethanol and finally dried in a vacuum desiccator over anhydrous calcium chloride. Co(II) and Ni(II) complexes were isolated in the presence of sodium acetate as a buffering agent. The pyridine complexes were prepared by adding an excess of pyridine to the solid appropriate complexes. The complexes were filtered off and washed thoroughly using absolute ethanol or diethylether.

Physical measurements

Electronic spectra in DMSO were recorded on a Pye Unicam SP 1800 spectrophotometer. Infrared spectra were measured using a Pye Unicam SP 2000 spectrophotometer. magnetic resonance spectra were recorded on a Varian EM-360 (60 MHz) spectrophotometer. The values of molar conductance were measured using a Tacussel conductivity bridge type CD6NG in DMSO at room temperature (25°). Magnetic moments were at Alexandria University using a Gouy balance and $HgCo(NCS)_4$ as calibrant.

Analyses

The metal and halide contents were analysed by standard methods.[12] Carbon and hydrogen contents were analysed by the Microanalytical Unit of Mansoura University, Egypt.

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