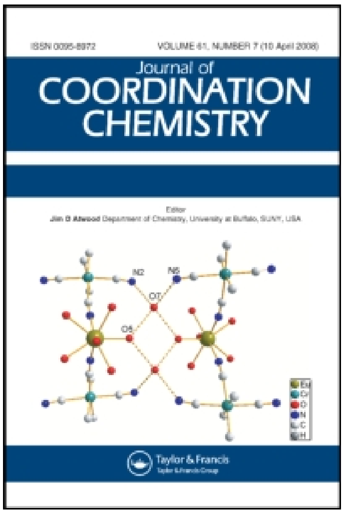

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NEW METAL COMPLEXES DERIVED FROM 1-ACETYL-TRIMETHYLAMMONIUM CHLORIDE-4-PHENYL-3-THIOSEMICARBAZIDE WITH SOME DIPOSITIVE METAL IONS

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The preparation and characterization of some dipositive metal ion complexes derived from 1-acetyl-trimethylammonium chloride-4-phenyl-3-thiosemicarbazide [(ATPTS)]Cl is reported. The solid complexes with the composition $[M(ATPTS)X_2]Cl.nH_2O$, (M=Mn(II), Cu(II), Zn(II) and Hg(II); X=Cl, Br, $\frac{1}{2}SO_4$, Ac or NO_3 and n=0-3), $[M(ATPTS)_2X_2]Cl_2$, (M=Ni(II), Cu(II) and Cd(II); X=Cl,Br), $[Co(ATPTS)Cl(H_2O)]Cl_2.H_2O$ and $[Cu(ATPTS)SO_4Py_2]Cl$, have been characterized on the basis of elemental analyses and spectra (IR, visible and NMR), as well as magnetic and conductivity measurements. IR spectral data indicate that the ligand coordinates *via* the carbonyl oxygen or thiocarbonyl sulphur atoms and the appropriate hydrazide nitrogen atom to give a 5-membered chelating ring.

INTRODUCTION

In continuation of our earlier work[1-5] on ligands containing the thiosemicarbazide group, we report herein the preparation and characterization of new metal complexes derived from ATPTS with some dipositive metal ions. The stereochemistry of the isolated complexes has been determined with the help of spectral and magnetic measurements.

RESULTS AND DISCUSSION

All the metal complexes (Table 1) are stable in air and partially soluble in most common organic solvents but easily soluble in DMF and DMSO except the Ni(II) complex which is insoluble in all organic solvents tried. The molar conductivity of uncomplexed ATPTS (55 $ohm^{-1}cm^2mole^{-1}$) in DMF at 25° falls in the range reported for uni-univalent electrolytes,[6] indicating that the chloride ion is readily ionized in DMF and therefore the ligand can be represented by structure (I).

(I)

The molar conductivities of the metal complexes in DMF are found in ranges which have been reported for 1 : 1 or 1 : 2 electrolytes.[6,7] The high value (125 $ohm^{-1}cm^2 mole^{-1}$) of the Co(II) complex suggests the presence of two chloride ions in the outer sphere and therefore the possibility of a coordinated water molecule as is indicated in Table 1.

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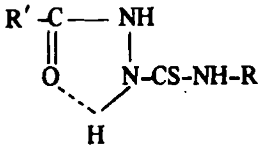
TABLE I
Analytical data and other physical properties.

Compound	M.P. (°)	Colour	% Calc.				% Found				Molar Cond. in DMF
			C	H	X	M	C	H	X	M	
ATPTS	202	white	47.60	6.32	11.71	–	47.50	6.40	11.60	–	55
$[Cu(ATPTS)Cl_2]Cl$	235	yellowish-green	32.96	4.38	24.32	14.53	32.69	3.85	24.49	15.05	58
$[Cu(ATPTS)_2Br_2]Cl_2$	135	dark brown	34.77	4.62		7.66	34.94	4.16		7.92	115
$[Cu(ATPTS)SO_4Cl\cdot 2H_2O$	225	grey	28.91	4.65		12.74	28.81	3.92		12.90	65
$[Cu(ATPTS)Ac_2]Cl\cdot 3H_2O$	242	yellowish-green	35.68	5.80		11.80	35.62	5.51		12.00	55
$[Cu(ATPTS)(NO_3)_2]Cl$	>280	dark grey	29.39	3.90		12.95	30.22	3.47		12.70	50
$[Co(ATPTS)Cl(H_2O)]Cl_2\cdot H_2O$	>280	olive-green	30.75	4.94	22.69	12.57	29.99	4.95	22.50	12.23	125
$[Ni(ATPTS)_2Cl_2]Cl_2$	>280	red	39.20	5.21	14.46	7.98	39.95	5.23	15.00	8.09	
$[Hg(ATPTS)Cl_2]Cl$	229	white	25.11	3.33	18.53	34.86	25.30	3.50	18.60	37.74	50
$[Zn(ATPTS)Cl_2]Cl$	233	white	32.81	4.36	24.21	14.91	32.66	4.56	24.41	14.71	58
$[Mn(ATPTS)Cl_2]Cl$	258	yellow	33.62	4.46	42.81	12.81	33.40	4.32	24.50	13.00	81
$[Cd(ATPTS)_2Br_2]Cl_2$	195	white	32.83	4.36		12.80	32.50	4.21		12.50	120
$[Cu(ATPTS)SO_4Py_2]Cl$	>280	dark green	42.90	4.50		10.40	42.71	4.40		10.27	125

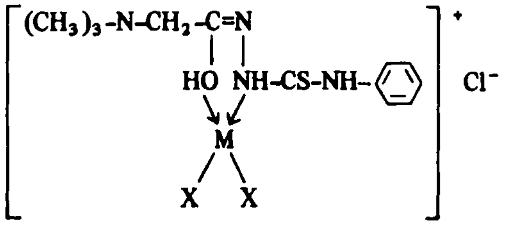
The infrared spectrum of uncomplexed ATPTS shows two bands at 1680 and 1700 cm^{-1} which are assigned to hydrogen bonded and free carbonyl groups respectively. Also, the band at 1240 cm^{-1} may be assigned to ν_{CS} of a thiocarbonyl group. No bands were observed above 3500 cm^{-1} or in the region 2600-2550 cm^{-1}. All these observations indicate that the ligand exists mainly in the keto form (I). The presence of two broad weak bands at *ca.* 2140 cm^{-1} and 1870 cm^{-1} which are due to N-H- - - O stretching and bending vibrations[8] may suggest the presence of intramolecular hydrogen bonding (structure II).



(II) R = phenyl and R' = $(CH_3)_3\overset{\overset{Cl^-}{|}}{N^+}CH_2$

The disappearance of the carbonyl band on complexation in the spectra of all complexes except those of Cu(II) bromide, Cd(II) and Hg(II) chloride with the simultaneous appearance of new bands at 1550 and 1080 cm^{-1}, which were assigned respectively to $N\text{---}C\text{---}O$[9] and (C–O) vibrations, may be taken as an evidence for participation of the (C–O) group in bonding. The enolization of the carbonyl group takes place through the adjacent (NH) group. The exceptions above show a decreases in ν_{CS} indicating that the thioketo group acts as a coordination site.

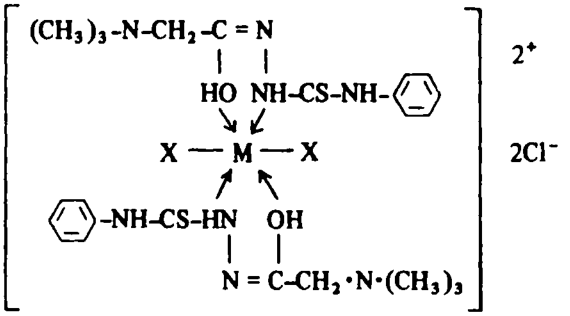
The ν_{NH} bands at 3470, 3230 and 3140 cm^{-1} in the spectrum of the ligand show a negative shift in the spectra of all complexes indicating the participation of the (NH) groups in bond formation. The small positive shift (10-15 cm^{-1}) of the band at 1000 cm^{-1} assigned[10] to ν_{N-N} in the spectrum of the ligand may be taken as an evidence for the participation of at least one of the (NH) groups in bonding. The appearance of a new band in the low frequency region at 350 cm^{-1} attributed[11] to ν_{M-N} in the spectra of the complexes lends support for the participation of one of the (NH) groups in bonding. Also, the appearance of new bands at 1340 and 410 cm^{-1} attributed[12,13] to (OH) deformation and ν_{M-O} lend support for structures (III) and (IV). Strong evidence for the presence of a free (OH) group in the coordinated ligand comes from proton magnetic resonance measurements of solution of the diamagnetic complexes in d_6-DMSO. In, for example, a solution of $[Zn(ATPTS)Cl_2]$ Cl, the (OH) proton signal at 9.35 ppm, downfield from TMS, disappears upon addition of D_2O. Studies of the Cd(II) and Hg(II) complexes did not reveal such an (OH) group which suggests that the ligand coordinates in the keto form.



(III)

M = Mn(II), Cu(II), Zn(II)

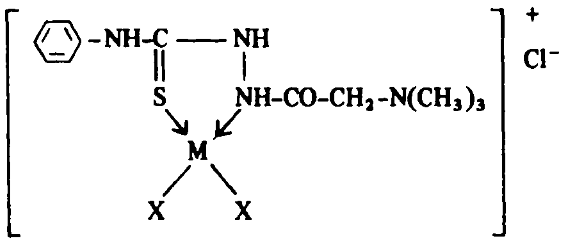
X = Cl, ½SO_4, NO_3, Ac



(IV)

M = Ni(II), Cu(II)
X = Cl, Br

The position of the bands associated with the thioketo group[14] at 1240 and 760 cm^{-1} remains unchanged in the spectra of most complexes, but both bands are shifted to lower wavenumbers in case of complexes of Cu(II) bromide, Cd(II) and Hg(II) chloride. The negative shift of the thioketo group (30–40 cm^{-1}) for these complexes suggests that it acts as a bonding atom as shown in structure (V).



(V)

M = Cu(II), Cd(II), Hg(II)
X = Cl, Br

The new band observed at 450 cm^{-1} due[15] to ν_{M-S} can be taken as additional evidence for this structure.

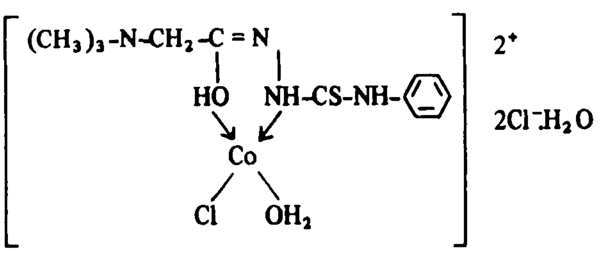
The pyridine complex of Cu(II) shows bands at 3040, 1015, 910 and 710 cm^{-1} due to (C–H) stretching and deformation vibrations. Also, the bands at 1615 and 1530 cm^{-1} attributed[16] to $\nu_{C=C}$ and $\nu_{C=N}$ suggests the presence of pyridine molecules coordinated to the Cu(II) ion.

The structures of the metal complexes can be assigned on the basis of electronic spectra in solution (DMSO and pyridine) and are confirmed by magnetic measurements. The results are shown in Table 2. The value of the magnetic moment for the Co(II) complex is found to be 4.65 B.M., which suggests a tetrahedral geometry for the Co(II) ion. The electronic spectrum in DMSO exhibits three absorption bands at 14,749, 16,077 and 18,050 cm^{-1}. The strong band at 14,749 cm^{-1} is assigned to the $^4A_2 \rightarrow {}^4T_1$ (p) transition, while the band at 18,050 cm^{-1} may be assigned to a spin-forbidden transition.[17] This spectrum is very similar to those reported for other pseudo-tetrahedral Co(II) structures. Structure (VI) is proposed for the Co(II) complex on the basis of its molar conductance (125 ohm^{-1} cm^2 mole^{-1}) and the infrared spectra together with the electronic spectra and magnetic data.

TABLE II

Spectral and magnetic properties of the ATPTS complexes.

Compound	μ_{eff} (B.M.)	Medium	Electronic Spectra (in cm^{-1})
$[Co(ATPTS)Cl(H_2O)]Cl{\cdot}H_2O$	4.65	DMSO	14,749, 16,077, 18,050
		pyridine	12,195, 14,500, 18,180, 18,868
$[Cu(ATPTS)Cl_2]Cl$	2.02	DMSO	12,494(br), 17,000(sh), 21,425
		pyridine	13,513
$[Cu(ATPTS)SO_4]Cl{\cdot}2H_2O$		DMSO	14,705
		pyridine	14,000(sh), 15,400(br)
$[Cu(ATPTS)Ac_2]Cl{\cdot}3H_2O$		DMSO	14,700
		pyridine	13,900
$[Cu(ATPTS)(NO_2)_2]Cl$		DMSO	13,700
		pyridine	13,940
$[Cu(ATPTS)_2Br_2]Cl_2$	1.78	DMSO	12,160(sh), 13,700(br)
$[Ni(ATPTS)_2Cl_2]Cl_2$		DMSO	12,195, 14,300, 19,230, 29,585



(VI)

The bands observed at 3500, 1610, 890 and 770 cm^{-1} in the IR spectrum of the Co(II) complex are assigned respectively to $\nu(OH)$, $\nu(H_2O)$, $Q_r(H_2O)$ and $Q_w(H_2O)$ vibrations[18] and indicate the presence of coordinated water molecules. On drying this complex *in vacuo* or by heating in an oven up to 120°, only one of its water molecules is removed which may indicate the presence of one molecule of water in the coordination sphere. Dissolution of the Co(II) complex in pyridine turns its colour from green to brownish-red and the spectrum exhibits bands at 12,195, 14,500, 18,180 and 18,868 cm^{-1}. These values are different from those observed in DMSO and are similar to those reported for six coordinate pyridine adducts of Co(II).[19]

The spectrum of the Ni(II) complex in DMSO exhibits three absorption bands at 12,195, 19230 and 29,585 cm^{-1} which are assigned respectively to $^3A_{2g} \rightarrow {^3T_{2g}}$ (ν_1), $^3A_{2g} \rightarrow {^3T_{1g}}$ (F) (ν_2) and $^3A_{2g} \rightarrow {^3T_{1g}}$ (P) (ν_3) transitions in octahedral geometry.[20] The ratio ν_2/ν_1 lies in the range 1.55-1.56[21-22] and therefore can be taken as an additional evidence for the proposed octahedral structure.

The spectra of the Cu(II) sulphate, acetate and nitrate complexes are all similar and exhibit a broad band centred at *ca.* 14,000 cm^{-1} which is assigned to the $^2B_{1g} \rightarrow {^2A_{1g}}$ transition in a square planar configuration.[23-24] The Cu(II) chloride complex shows two bands at 19,600 and 12,494 cm^{-1} indicating in this case a pseudo-tetrahedral geometry at the Cu(II) ion. The band at 19,600 cm^{-1} may be assigned to a Cl → Cu charge transfer. The structure is confirmed by the magnetic moment (2.02 B.M.). The electronic spectrum and magnetic moment (1.78 B.M.) for the Cu(II) bromide complex are in good agreement with those reported for octahedral cases. The solution spectra in pyridine of the Cu(II) complexes were also recorded, and exhibit a broad strong band in the region 13,513-

14,090 cm^{-1} with a more or less pronounced low energy shoulder. This may be due to the $^2E_{1g} \rightarrow {}^2T_{2g}$ transition, indicating a distorted octahedral structure around the central Cu(II) ion.[25]

EXPERIMENTAL

All chemicals used were of analytical grade. The ligand (I) was prepared by slowly adding phenyl isothiocynate (13.5 ml) to a solution of Girard's reagent T (acetylhydrazide trimethylammonium chloride) in absolute ethanol. The mixture was refluxed on a water bath for 15 minutes. The white product was crystallized several times from absolute ethanol and dried in a vacuum desiccator over anhydrous calcium chloride. The purity of the ligand was checked by elemental analysis and NMR (M.P., 202°). The solid complexes were prepared by adding equimolar amounts of ligand and a metal salt in absolute ethanol. The reaction mixture was refluxed on a water bath for about 1 hr. and then concentrated until precipitation occurred. The product was filtered, washed several times with hot ethanol and dried in a vacuum desiccator. The pyridine adduct of the Cu(II) sulphate complex was prepared by adding an excess of pyridine in the cold to the solid complex. Elemental analyses were performed by the Microanalytical Unit of Mansoura University. The metal and halide contents were determined by standard methods.[26]

Electronic solution spectra of the complexes in DMSO and pyridine were recorded on a Pye Unicam SP-1800 spectrophotometer. Infrared spectra were recorded on a Pye Unicam SP-2000 spectrophotometer. Molar conductance values were measured using a Tacussel conductivity bridge (type CD6NG) in DMSO at 25°. The magnetic moment measurements were carried out at Alexandria University using a Gouy balance and $Hg[Co(SCN)_4]$ as the calibrant. Diamagnetic corrections were made using Pascal's constants. Proton magnetic resonance spectra were measured on a Varian EM-360 (60 MHz) spectrophotometer.

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