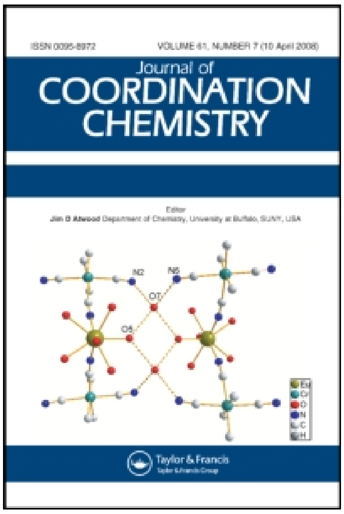

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COMPLEXES OF IMIDAZOLINE-2-THIONE AND ITS 1-METHYL ANALOGUE WITH Cu(II), Zn(II), Cd(II) AND Hg(II) SALTS

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The reaction of Cu(II), Zn(II), Cd(II) and Hg(II) chlorides and bromides with imidazoline-2-thione (IZT) and its *N*-methyl derivative (NMIZT) yields complexes of stoichiometry ML_2X_2 and ML_2X (IZT) and its *N*-methyl derivative (NMIZT) yields complexes of stoichiometry ML_2X_2 and ML_2X (where M = Cu(I)); copper(II) halides yield Cu(I) complexes. On the basis of infrared and ^{13}C n.m.r.

INTRODUCTION

The current interest in the coordination chemistry of thione derivatives of various heterocyclic molecules arises from the wide ranging application of heterocyclic *S*, *N*-containing molecules in industry[1,2] and medicine[3,4] and the diverse donor characteristics exhibited by them towards various metal ions.[5] The present work is devoted to complexes originating from the interaction of chloride and bromide salts of Cu(II), Zn(II), Cd(II) and Hg(II) with imidazoline-2-thione (IZT) and 1-methylimidazoline-2-thione (NMIZT). The complexes obtained have been studied by means of infrared and ^{13}C n.m.r. spectroscopy. Complexes of Co(II) and Zn(II) salt with IZT and NMIZT have been reported recently by Raper *et al.*[5,6] Coordination exclusively *via* sulfur was inferred for NMIZT while bonding through both sulfur and nitrogen was postulated for IZT.[5] The purpose of this work was to reexamine the infrared assignments of IZT and NMIZT, discuss the perturbation of the ligand bands on coordination to metal ions and to provide ^{13}C n.m.r. data which gives more conclusive information concerning the coordination site.

EXPERIMENTAL

IZT was synthesized and purified according to the literature method.[7] NMIZT (Aldrich) was recrystallised from chloroform. The metal complexes were obtained by dropwise addition of ethanol solution of the metal halide (1 mmol in 10 cm^3) to a stoichiometric amount of the ligand in ethanol (2 mmol in 50 cm^3) and refluxing the solution for 0.5 h on a water bath. The copper complexes were obtained at room temperature. The products obtained on cooling were washed with ethanol and dried *in vacuo* over P_2O_5.

Microanalysis were carried out in the Microanalytical Laboratory of the Department and the metal contents were determined by standard methods. The analytical results are shown in Table 1.

Infrared spectra (4000-200 cm^{-1}) were recorded as Nujol mulls between cesium iodide plates and also as KCl pellets (4000-400 cm^{-1}) on a Perkin-Elmer 599 spectrophotometer.

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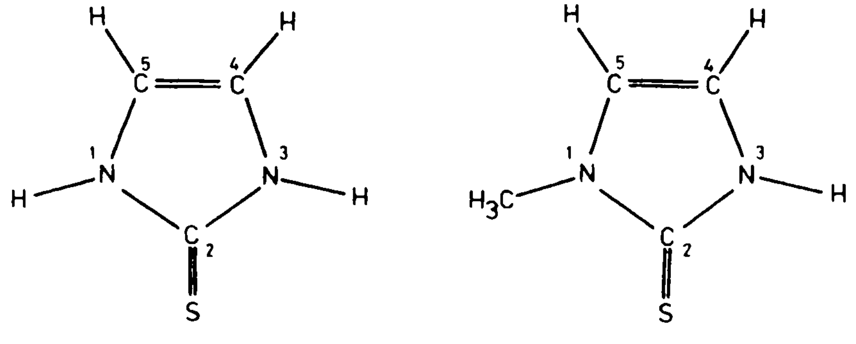

(IZT) (NMIZT)

FIGURE (I)

The spectra were calibrated with standard frequencies of polystyrene. ^{13}C n.m.r. spectral measurements were made on a Bruker WH 270 spectrometer at 67.89 MHz using d^6-DMSO as the solvent which also served as the lock. However, the reported values are quoted with respect to TMS.

RESULTS AND DISCUSSION

The reaction of copper(II) halides with the ligands initially yielded a brown solution which finally precipitated pale yellow complexes. The magnetic measurements confirmed

TABLE 1
Analytical results

Complex[a]		Found (calcd) %			
		C	H	N	Metal
CuL_2Cl	Pale yellow	24.0 (24.0)	2.6 (2.7)	18.6 (18.7)	21.2 (21.3)
CuL_2Br	Pale yellow	20.9 (21.0)	2.2 (2.3)	16.2 (16.3)	18.4 (18.5)
ZnL_2Cl_2	Colourless	21.4 (21.4)	2.4 (2.4)	16.5 (16.7)	19.2 (19.4)
ZnL_2Br_2	Colourless	17.0 (17.0)	1.8 (1.9)	13.0 (13.2)	15.2 (15.4)
CdL_2Cl_2	Colourless	18.7 (18.8)	2.0 (2.0)	14.4 (14.6)	29.3 (29.3)
CdL_2Br_2	Colourless	15.2 (15.2)	1.6 (1.7)	11.8 (11.9)	23.8 (23.8)
HgL_2Cl_2	Colourless	15.1 (15.3)	1.7 (1.7)	11.8 (11.9)	42.1 (42.5)
HgL_2Br_2	Colourless	12.7 (12.8)	1.3 (1.4)	9.9 (10.0)	35.2 (35.8)
CuL'_2Cl	Grey	29.3 (29.4)	3.7 (3.7)	17.0 (17.1)	19.4 (19.4)
CuL'_2Br	Pale yellow	25.8 (25.8)	3.1 (3.2)	15.0 (15.1)	17.1 (17.1)
ZnL'_2Cl_2	Colourless	26.4 (26.4)	3.2 (3.3)	15.3 (15.4)	17.6 (17.9)
ZnL'_2Br_2	Colourless	21.1 (21.2)	2.6 (2.6)	12.2 (12.4)	14.3 (14.4)
CdL'_2Cl_2	Colourless	23.3 (23.3)	2.8 (2.9)	13.5 (13.6)	27.3 (27.3)
CdL'_2Br_2	Colourless	19.2 (19.2)	2.3 (2.4)	11.1 (11.2)	22.5 (22.5)
HgL'_2Cl_2	Colourless	19.2 (19.2)	2.3 (2.4)	11.0 (11.2)	39.9 (40.1)
HgL'_2Br_2	Colourless	16.1 (16.3)	1.9 (2.0)	9.4 (9.5)	33.9 (34.1)

[a] L = IZT, L' = NMIZT.

the metal to be present as copper(I). The oxidation of the thiourea class of compounds by copper(II) salts is well documented.[8,9] The complexes show a tendency to turn green in the course of time and in solvents such as DMSO.

Previous spectroscopic studies on the free ligands rule out the existence to any significant extent of the compounds in thiol form. It is generally assumed that with thioamide ligands, coordination to the metal occurs through sulfur, although alternate modes of bonding through nitrogen or through both nitrogen and sulfur are possible. It is well known that Cu(I), being a typical class b metal, forms strong bonds with soft ligands, such as sulfur. The very rapid reduction of Cu(II) demonstrates the much stronger interaction of a soft donor ligand with the soft metal Cu^+, than with the hard Cu^{2+}.

Infrared Spectra

Selected infrared absorptions of the free ligands and complexes are shown in Table 2. The assignment of the bands in Table 2 is made by comparison with those of imidazolidine-2-thione[10,11] (commonly referred to as ethylene thiourea, etu), 1, 3, 4, 6-tetrahydropyrimidine-2-thione[12] (tpt), imidazole[13] and *N*, *N'*-dimethylthiourea[14] whose detailed assignments have recently become available. Further support has been obtained from *N*, *N'*-dideuteration as well as *S*-methylation of the free ligands. The assignments of Raper *et al*[5,6] for IZT and NMIZT based on the empirical assignments of Singh and Rivest[15] need revision in view of the recently available work on related molecules referred to above.

The coordination of the ligands through the nitrogen atom would require a downward shift in the sensitive N-H stretching frequency by 200-300 cm^{-1}. However, the spectra of complexes of both IZT and NMIZT reveal a significant upward shift of 20 to 80 cm^{-1} relative to the frequencies of the free ligands in solids. This suggests that we can exclude nitrogen as the coordinating atom. A comparison of the spectra of the ligands in the solid state and in solution shows the N-H stretching absorption lowered by nearly 350 cm^{-1} in the solid due to the presence of intermolecular N-H . . . . S hydrogen bonding. The shift in the N-H stretching frequency is essentially due to two factors; (*i*) variation in the hydrogen bonding interactions and (*ii*) a change in the positive charge on the nitrogen atom upon coordination with increasing double bond character of the C-N grouping. An increasing positive charge on nitrogen would lower the N-H stretching frequency as would the stronger hydrogen bonding interactions.

A coupled band arising from N-H bending and C-N stretching (thioamide II band) at 1482, 1460 cm^{-1} is shifted to higher frequencies on complexation, indicating an increase in the double bond character of the C-N bond and coordination through sulfur. Support for *S*-coordination would be obtained from the position of $\nu_{C=S}$ absorption. More realistic assignments should involve absorptions in the 700-500 cm^{-1} range which shift towards lower wave numbers in the complexes. The $\nu_{C=S}$ vibration in etu is assigned to 507 cm^{-1} by comparison with spectra of the selenium analogue, effects of *S*-methylation, and normal vibration analysis.[10,11] In the ligands IZT and NMIZT the medium intensity bands at 520 and 532 cm^{-1} are akin to the 507 cm^{-1} band of etu. These bands for the ligands are displaced towards lower energy by 20-35 cm^{-1} in the complexes and could be ascribed to a vibration involving substantial C = S stretching. The assignment of C = S deformations are made on the basis of the assignments in etu.

The above assignment of thioureide absorptions is supported by the spectra of the *S*-methyl compounds obtained by reacting the ligands with methyliodide. On *S*-methylation, which diminishes the double bond character of the C = S bond and increases the double bond order of the C-N bond, the 520 cm^{-1} band of IZT and 532 cm^{-1} band of NMIZT is displaced to the lower energy of 490 cm^{-1} and the C-N stretching mode around 1460 cm^{-1} shows an upward shift to around 1530 cm^{-1}.

TABLE 2
Selected infrared absorptions (cm^{-1})

	ν_{NH}	ν_{CN}	δ_{NH}	π_{NH}	$\nu_{C=S}$	$\delta_{C=S}$	$\pi_{C=S}$	ν_{M-S}	$\nu_{M-Cl/Br}$
L (=IZT)	3140 s sh 3100 s	1482 s	1420 w sh 1230 s	832 ms	520 mb	340 s	250 m	–	–
CuL_2Cl	3180 s sh 3120 mb	1500 w	1420 w sh 1230 m	762 ms	495 ms	360 m	285 m	320 w	250 w
CuL_2Br	3150 sb 3120 s	1505 w	1410 w 1230 s	800 s	495 ms	355 m	295 w	320 w	270 w
ZnL_2Cl_2	3180 sh 3120 s	1500 w	1410 w 1235 ms	790 ms	500 ms	365 m	290 m	290 m	260 m
ZnL_2Br_2	3240 s 3120 sb	1490 s sh	1410 w sh 1225 ms	760 s sh	500 ms	360 m	270 w	290 w	240 w
CdL_2Cl_2	3220 s 3160 m	1510 m sh	1410 w 1235 m	780 s	500 s	350 s	360 ssh	270 m	240 m
CdL_2Br_2	3220 sb 3160 sb	1510 wsh	1400 w 1210 m	780 s	495 s	360 s	270 w	300 wsh	230 w
HgL_2Cl_2	3160 s 3140 mb	1510 wsh	1410 m 1220 m	770 ms	495 s	380 m	250 m	290 w	240 w
HgL_2Br_2	3240 sb 3160 s	1482 s	1410 m 1220 m	760 m	490 ms	380 m	260 w	300 w	240 w
L′ (=NMIZT)	3090 mb	1460 s	1242 s	765 s	532 ms	412 ms	255 ms	–	–
CuL'_2Cl	3120 mb	1470 s	1250 s	750 s	510 ms	410 ms	275 m	310 w	260 ssh
CuL'_2Br	3090 ms	1490 ssh	1250 w	765 s	500 ms	410 ms	285 ms	320 s	295 ms
ZnL'_2Cl_2	3140 ms	1480 ssh	1280 ms	730 ms	515 ms	405 ms	290 mb	320 m	280 mb
ZnL'_2Br_2	3120 w	1470 sb	1280 m	740 ms	515 ms	400 ms	300 m	320 m	250 m
CdL'_2Cl_2	3120 ms	1490 s	1255 w	750 ssh	510 ms	412 ms	260 ms	310 w	285 ms
CdL'_2Br_2	3120 mb	1465 s	1255 ms	735 s	512 s	412 s	290 ms	305 s	240 ms
HgL'_2Cl_2	3100 ms	1480 s	1245 ssh	750 s	510 ms	410 ms	300 ssh	320 ms	250 w
HgL'_2Br_2	3200 sb	1465 s	1255 w	750 s	510 s	410 s	290 w	310 ms	230 w

TABLE 3

^{13}C n.m.r. data (δ in ppm from TMS)

Compound[a]	C(2)	C(4)	C(5)	CH_3
IZT	160.37	115.39		
CdL_2Cl_2	156.59	116.32		
CdL_2Br_2	154.94	116.72		
HgL_2Cl_2	150.45	117.93		
HgL_2Br_2	150.42	116.97		
NMIZT	160.65	114.20	119.29	34.26
CdL'_2Cl_2	155.97	115.26	120.69	34.00
CdL'_2Br_2	156.34	115.20	120.59	34.07
HgL'_2Cl_2	150.60	116.90	122.30	34.54
HgL'_2Br_2	150.94	116.84	122.20	34.66

[a] L = IZT, L' = NMIZT.

The bands at 832 cm^{-1} in IZT and at 765 cm^{-1} in the *N*-methyl derivative, easily recognized from its broad nature and sensitivity to *N*-deuteration (which shifts the bands to 570 and 550 cm^{-1} respectively) by exchange with D_2O, can be attributed to an out of plane N-H deformation. It is displaced 15-70 cm^{-1} in the metal complexes. Similar frequency shifts have been described in the literature for complexes of etu,[16] tpt[12] and related ligands.[17-19] It is noteworthy that none of the bands in the 780 cm^{-1} range are displaced on complexation or *S*-methylation which allows us to revise the assignment of Raper *et al.*

Below 400 cm^{-1} some new absorptions which could be assigned to M-S and M-Cl(Br) stretching vibrations are found in the spectra of the complexes. A tentative assignment of these modes is included in Table 2.

^{13}*C n.m.r. Spectra*

More conclusive evidence concerning the coordination sites is provided by the ^{13}C n.m.r. spectra. The ^{13}C n.m.r. assignments are summarised in Table 3. The carbon nearest to sulfur should be expected to be the most sensitive to coordination. It is found in fact that the important changes in values affect the thiocarbonyl carbon which is shifted upfield. This result leads us to conclude that the coordination occurs *via* sulfur in all compounds. The magnitude of the shifts appears to be in agreement with the HSAB principle. The observation of a downfield shift of a smaller magnitude for the C-H carbons is in accord with this conclusion.[20] This may be due to the increase in the double bond character of the C-N linkage upon coordination of sulfur. Spectra of Cu(I) and Zn(II) complexes could not be recorded owing to their low solubility.

By comparison with analogous complexes of etu and thiazolidine-2-thione whose X-ray supported structures are available[21,22] the Zn(II), Cd(II) and Hg(II) complexes may be postulated to have tetrahedral geometry while the Cu(I) complexes have a dimeric structure.

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