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Note

INFRARED AND THERMAL STUDIES OF 1,10-PHENANTHROLINE-MONO-*N*-OXIDE CHELATES OF ZINC(II) AND CADMIUM(II)

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Considerable attention has recently been focussed on the coordination behaviour of aromatic amine-*N*-oxides [1–3]. Due to the different ligating behaviour of aromatic amine-*N*-oxides it was considered of interest to study the coordination behaviour of 1,10-phenanthroline-mono-*N*-oxide (PhenNO) towards Zn(II) and Cd(II). The ligand is rigidly held in a *cis* configuration in the crystal and functions as an essentially planar chelating agent [4]. Some transition and non-transition metal chelates of PhenNO have already been reported [5–11].

EXPERIMENTAL

The ligand was prepared from 1,10-phenanthroline by the method of Corey et al. [7]. The metal salts and other chemicals used were of B.D.H. AR grade or Merck extra pure grade.

All the compounds were obtained by adding ethanolic solutions of the ligand to a solution of the zinc or cadmium salts in ethanol in a 2 : 1 molar ratio and stirring at room temperature. The respective complexes precipitated immediately; these were filtered, washed with ethanol and dried in vacuum.

The interaction of zinc(II) and cadmium(II) salts with PhenNO results in the formation of compounds having the composition MX_2L_2 (M = Zn(II) or Cd(II); X = Cl, Br, I, NCS or CH_3COO) (Table 1). The analytical data indicate that the compounds are pure. The conductance values of the compounds in nitrobenzene are consistent with their non-electrolytic nature (Table 1). The molecular weights in freezing nitrobenzene also support the similar electrolytic behaviour of the compounds. All the complexes are diamagnetic as expected for a d^{10} system.

TABLE 1

Analytical, conductivity and partial IR data (cm^{-1}) for PhenNO chelates of zinc(II) and cadmium(II)

Compound	M%		N%		Anion%		Ω_m(ohm^{-1} cm^{-2} mol^{-1})	ν(N–O)	ν(N–O)	ν(M–O)	ν(M–N)
	Found	Calc	Found	Calc	Found	Calc					
PhenNO	–	–	–	–	–	–	–	1270s 1250s	810m	450m	390m
$ZnCl_2 \cdot 2PhenNO$	12.16	11.94	10.39	10.29	13.16	13.05	3.6	1230s 1210m	815m	435m	380m
$ZnBr_2 \cdot 2PhenNO$	10.42	10.26	8.92	8.84	25.38	25.27	3.9	1235s 1215m	815m	440m	395m
$ZnI_2 \cdot 2PhenNO$	9.12	8.94	7.81	7.70	35.04	34.93	5.1	1230s 1215m	810m	450m	395m
$Zn(NCS)_2 \cdot 2PhenNO$	11.19	11.03	14.37	14.26	19.79	19.69	5.3	1220s 1210m	815m	435m	390m
$Zn(CH_3COO)_2 \cdot 2PhenNO$	11.18	10.99	9.56	9.47	–	–	4.9	1225s 1210sh	815m	440m	395m
$CdCl_2 \cdot 2PhenNO$	19.16	18.95	9.57	9.49	12.13	12.01	4.1	1220s 1210m	810m	445m	390m
$CdBr_2 \cdot 2PhenNO$	16.62	16.47	8.34	8.23	23.65	23.52	4.9	1225s 1210m	815m	445m	395m
$CdI_2 \cdot 2PhenNO$	14.60	14.47	7.34	7.23	32.93	32.81	5.8	1225s 1215m	820m	450m	390m
$Cd(SCN)_2 \cdot 2PhenNO$	17.80	17.61	13.31	13.20	18.34	18.23	5.3	1225s 1210m	815m	440m	395m

Infrared spectra

Table 1 records the important IR bands for the ligand and its complexes with Zn and Cd. The free ligand exhibits a rich spectrum in the 1600–200 cm^{-1} region [5,6] which undergoes characteristic frequency shifts upon metal complex formation. The (N–O) stretching frequency, observed at 1270 and 1250 cm^{-1} in the free ligand, is shifted towards lower frequencies in the complexes due to coordination of the oxygen atom of the ligand to the metal ion [1–3]. The (N–O) bending in the free ligand, observed at ca. 810 cm^{-1} exhibits a small shift in the spectra of the complexes as expected [1–3]. Coordination through the pyridine fragment nitrogen atom is suggested by the frequency shifts and splitting of the several IR bands associated with the vibration of this fragment [5,13–16]. Absorptions associated with C–H out-of-plane deformation modes, as expected, undergo slight positive shifts due to tightening of the aromatic ring on complexation [1–3]. In the far IR region, ν(M–O) and ν(M–N) have been identified. The overall IR spectral evidence suggests that the ligand acts as a bidentate O,N-chelating agent forming a six-membered ring with the metal ions.

The positions of the M–Cl stretching mode [17–19] in the chloro complexes of zinc and cadmium with PhenNO strongly suggest octahedral environments of the two bidentate ligand molecules and terminally bonded chlorine atoms in these complexes. The ν(M–Br) and ν(M–I) could not be observed because they absorb below the frequency limit of the spectrometer used in the present studies.

In the $Zn(NCS)_2 \cdot 2PhenNO$ complex some new absorption bands at 2085, 860 and 485 cm^{-1} are observed, which are identified as the ν(CN), ν(CS) and δ(NCS) modes, respectively, due to coordinated thiocyanato groups. These frequencies are consistent with a terminally N-bonded isothiocyanato group [20]. The IR spectrum of the analogous cadmium complex shows bands at 2105, 760 and 420 cm^{-1} due to the ν(CN), ν(CS) and δ(SCN) modes, respectively, which clearly indicate an S-bonded thiocyanato group [20].

Thus, all the complexes of Zn(II) and Cd(II) presumably have an octahedral environment around them. In the case of Cd(II) the coordination number six is rather unusual. This once again confirms the view that the coordination number around a particular metal ion depends on the donor–acceptor characteristic of the participating ligand and metal [21].

Thermal studies

The results of thermal analyses are summarized in Table 2. The TG and DTG curves of the chelates show the absence of water molecules either in or out of the coordination sphere. All the chelates decompose endothermically in three steps. In the first step one mole of the ligand is lost and in the

TABLE 2

Thermal decomposition data of PhenNO chelates of zinc(II) and cadmium(II)

Compound	Decompn. temp. (°C)		Decompn. product	Wt. loss%		DTG peak
	Initial	Final		Found	Calc	
$ZnCl_3\cdot 2PhenNO$	180	215	$ZnCl_2\cdot PhenNO$	37.79	36.02	endo
	240	290	$ZnCl_2\cdot 0.5PhenNO$	55.41	54.04	endo
	490	550	ZnO	86.32	85.11	exo
$ZnBr_2\cdot 2PhenNO$	175	220	$ZnBr_2\cdot PhenNO$	32.06	30.96	endo
	230	280	$ZnBr_2\cdot 0.5PhenNO$	48.31	46.44	endo
	495	540	ZnO	89.10	87.20	exo
$Zn(NCS)_2\cdot 2PhenNO$	170	220	$Zn(NCS)_2\cdot PhenNO$	34.72	33.24	endo
	240	280	$Zn(NCS)_2\cdot 0.5PhenNO$	50.98	49.91	endo
	490	555	ZnO	88.42	86.24	exo
$Zn(CH_3COO)_2 \cdot 2PhenNO$	165	205	$Zn(CH_3COO)_2\cdot PhenNO$	34.32	33.16	endo
	240	280	$Zn(CH_3COO)_2\cdot 0.5PhenNO$	51.06	49.74	endo
	495	545	ZnO	87.32	86.29	exo
$CdCl_2\cdot 2PhenNO$	190	225	$CdCl_2\cdot PhenNO$	35.01	33.16	endo
	250	290	$CdCl_2\cdot 0.5PhenNO$	51.32	49.74	endo
	495	550	CdO	80.11	81.17	exo
$CdBr_2\cdot 2PhenNO$	185	230	$CdBr_2\cdot PhenNO$	30.16	28.82	endo
	255	290	$CdBr_2\cdot 0.5PhenNO$	44.96	43.23	endo
	490	555	CdO	83.20	81.17	exo
$Cd(SCN)_2\cdot 2PhenNO$	180	225	$Cd(SCN)_2\cdot PhenNO$	32.16	30.81	endo
	240	290	$Cd(SCN)_2\cdot 0.5PhenNO$	47.87	46.22	endo
	495	545	CdO	80.26	79.87	exo

second step only 0.5 mol of the ligand is lost, while finally at about 550°C the metal oxide is formed. If the lowest TG decomposition temperature is taken as a rough criterion of thermal stability, then the order of the stability of these complexes is: $Cl > Br > NCS > CH_3COO$.

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