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Note

INFRARED AND THERMAL INVESTIGATIONS OF 1,10-PHENANTHROLINE *N*,*N*′-DIOXIDE CHELATES OF ZINC(II) AND CADMIUM(II)

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Continuing our previous work [1] on mono *N*-oxides of 1,10-phenanthroline chelates of Zn(II) and Cd(II), the author reports herein on 1,10-phenanthroline *N*,*N*′-dioxide (phenNO_2) chelates of Zn(II) and Cd(II). The donor properties of phenNO_2 towards metal ions have been studied to a limited extent [2–5].

EXPERIMENTAL

The ligand was prepared by the method described for 2,2′-bipyridine *N*,*N*′-dioxide [6,7]. The metal salts and other chemicals used were of AnalaR or E. Merck grade.

The metal complexes were prepared by the following general method: 1 mmol of the metal salt in a suitable solvent was mixed with a solution of 3 mmol of the ligand in the same solvent. The reaction mixture was then stirred for ca. 3 h, when a precipitate was slowly thrown out, which was filtered, washed with the same solvent and finally with ether and dried in vacuo over P_4O_{10}.

The analyses, conductance, molecular weight and infrared spectra of the isolated complexes were obtained as reported previously [8] while TGA and DTA measurements were carried out by the method reported earlier [9].

RESULTS AND DISCUSSION

Stoichiometries of the newly-synthesised complexes were established on the basis of elemental analyses (Table 1). The compounds are not hygroscopic and are fairly stable at room temperature. All the complexes are non-electrolytes in nitrobenzene. The molecular weight measurements in nitrobenzene also support the similar electrolytic behaviour of the compounds.

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TABLE 1

Analytical, conductivity and partial IR data (cm^{-1}) for 1,10-phenanthroline *N,N'*-dioxide chelates of Zn(II) and Cd(II)

Compound	M (%)		N (%)		Anion (%)		Λ_m (ohm^{-1} cm^{-1} mol^{-1})	ν(N–O)	(N–O)	ν(M–O)
	Found	Calcd	Found	Calcd	Found	Calcd				
$phenNO_2$	–	–	–	–	–	–	–	1310s 1280s	855m	–
$ZnCl_2 \cdot 2phenNO_2$	12.10	11.60	10.32	10.00	12.91	12.67	4.3	1280s 1260m	860m	450m
$ZnBr_2 \cdot 2phenNO_2$	10.45	10.01	8.81	8.62	24.92	24.65	4.6	1285s 1270m	862m	440m
$ZnI_2 \cdot 2phenNO_2$	9.24	8.74	7.71	7.53	35.02	34.18	5.8	1290s 1275m	855m	435m
$Zn(NCS)_2 \cdot 2phenNO_2$	11.26	10.74	14.01	1388	19.71	19.17	5.1	1280s 1270m	860m	445m
$Zn(CH_3COO)_2 \cdot 2phenNO_2$	11.19	10.70	9.41	9.22	–	–	4.9	1285s 1275m	862m	440m
$CdCl_2 \cdot 2phenNO_2$	18.91	18.45	9.44	9.22	11.82	11.69	3.6	1280s 1270m	858m	430m
$CdBr_2 \cdot 2phenNO_2$	16.49	16.09	8.26	8.04	23.16	22.98	4.7	1290s 1275m	860m	425m
$CdI_2 \cdot 2phenNO_2$	14.51	14.17	7.28	7.08	31.66	32.15	5.9	1285s 1275m	860m	425m
$Cd(SCN)_2 \cdot 2phenNO_2$	17.52	17.17	12.97	12.88	18.01	17.79	4.9	1290s 1270m	855m	430m

Infrared spectra

The IR spectra of phenNO_2 and its metal complexes have been recorded in the 4000–200 cm^{-1} region. The relevant partial IR data are given in Table 1. The assignments are largely based on previous work on this ligand [2–5] and on the spectra of 2,2′-bipyridine *N,N′*-dioxide [10]. The strong absorptions at 1310 and 1280 cm^{-1} have been assigned to the characteristic N–O stretching vibration. A decrease in N–O stretching frequency on coordination to metal ions is observed. The bond formation between the metal ions and phenNO_2 presumably increases the electron demand of the donor oxygen atoms and so brings about a decrease of the N–O double bond character. The band observed at ca. 855 cm^{-1} can be ascribed to the N–O bending vibration; this undergoes little change on complex formation. The C–H out-of-plane vibrations which appear at 780 and 720 cm^{-1} shift to higher frequencies in metal compounds. This is due to the decrease in the electron density of the ring on complex formation [11]. The overall IR spectral evidence suggests that phenNO_2 acts as a bidentate *O,O*-chelating agent forming a seven-membered chelate ring with Zn(II) or Cd(II). The bands observed in all the chelates in the 450–420 cm^{-1} region are assigned as ν(M–O).

The ν(M–Cl) vibration has been assigned at ca. 275 cm^{-1}, while ν(M–Br) and ν(M–I) could not be assigned since they lie out of the region studied. In Zn(II) thiocyanate phenNO_2 chelate, the presence of bands at 2060 cm^{-1} (C≡N), 840 (C–S) and 460 cm^{-1} (δNCS) indicates the thiocyanate is N-bonded to zinc metal [12]. The IR spectrum of the $Cd(SCN)_2 \cdot 2phenNO_2$ chelate shows bands at 2110, 735 and 425 cm^{-1} due to ν(C≡N), ν(C–S) and δ(SCN) modes, respectively, which clearly indicates on S-bonded thiocyanate group [12].

Thermal studies

The results of the thermal analyses are summarised in Table 2. The TG and DTG curves of the chelates do not show the presence of water molecules either in or out of the coordination sphere. All the chelates decompose endothermically. All have two peaks, one *endo* and the other *exo*; the *exo* peak at the higher temperature is due to complete metal oxidation. The TG curves show that all the chelates complete their decomposition in three steps. In the first step 1 mol of ligand is lost, in the second step only 0.5 mol of ligand is lost and finally at 600°C metal oxide is formed. If minimum TG decomposition temperature is taken as a rough criterion of thermal stability, then the order of stability for the chelates studied herein is $Cl > Br > NCS > CH_3COO$.

TABLE 2

Thermal decomposition data for Zn(II) and Cd(II) chelates of 1,10-phenanthroline-*N*,*N*′-dioxide

Compound	Decomposition temp. (°C)		Decomposition product	Wt. loss		DTG peak
	Initial	Final		Found	Calcd.	
$ZnCl_2 \cdot 2phenNO_2$	210	235	$ZnCl_2 \cdot phenNO_2$	39.11	37.85	–
	270	410	$ZnCl_2 \cdot 0.5phenNO_2$	58.16	56.78	endo
	530	610	ZnO	86.89	85.53	exo
$ZnBr_2 \cdot 2phenNO_2$	205	230	$ZnBr_2 \cdot phenNO_2$	34.06	32.66	–
	260	405	$ZnBr_2 \cdot 0.5phenNO_2$	50.32	48.99	endo
	540	600	ZnO	89.06	87.51	exo
$Zn(NSC)_2 \cdot 2phenNO_2$	195	230	$Zn(NCS)_2 \cdot phenNO_2$	36.16	35.04	–
	250	400	$Zn(NCS)_2 \cdot 0.5phenNO_2$	53.82	52.56	endo
	530	590	ZnO	87.91	86.61	exo
$Zn(CH_3COO)_2 \cdot 2phenNO_2$	190	230	$Zn(CH_3COO)_2 \cdot phenNO_2$	36.12	34.92	–
	240	390	$Zn(CH_3COO)_2 \cdot 0.5phenNO_2$	54.01	52.38	endo
	540	605	ZnO	88.31	86.65	exo
$CdCl_2 \cdot 2phenNO_2$	215	240	$CdCl_2 \cdot phenNO_2$	35.72	34.92	–
	260	390	$CdCl_2 \cdot 0.5phenNO_2$	54.16	52.38	endo
	560	610	CdO	83.20	81.60	exo
$CdBr_2 \cdot 2phenNO_2$	210	245	$CdBr_2 \cdot phenNO_2$	31.91	30.45	–
	260	380	$CdBr_2 \cdot 0.5phenNO_2$	47.69	45.69	endo
	540	600	CdO	83.20	81.60	exo
$Cd(NCS)_2 \cdot 2phenNO_2$	200	240	$Cd(NCS)_2 \cdot phenNO_2$	34.06	32.51	–
	270	370	$Cd(NCS)_2 \cdot 0.5phenNO_2$	50.82	48.77	endo
	530	600	CdO	81.63	80.36	exo

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