Notes

polymerization of silicic acid is known to have a strong effect on such reactions [2], which could explain the lack of reaction in the synthetic mixture.

The IR spectra of SiT_n are markedly different from that of free tartaric acids. From an examination of the IR spectra of the free acid with that of its alkali metal salts it may be inferred that the bands at 1260, 1225, and 1197 cm⁻¹ in the former are associated with the carboxylic acid group, as they are not found in the spectra of the alkali metal salts. A similar comparison with succinic acid indicates the bands at 1140 and 1095 $\rm cm^{-1}$ should be associated with the secondary alcohol group of tartaric acid, as these are lacking in the spectrum of succinic acid. In SiT_n the 1260-1225-1197 cm⁻¹ trio is absent, while a large pronounced band appears at 1380 cm⁻¹, which is absent in the spectrum of the pure ligand. The antisymmetric stretching frequency of the carboxylic group at 1720 cm⁻¹, however is not appreciably affected by complex formation. The band at 1140 cm⁻¹ is slightly shifted to 1160 cm^{-1} in the SiT_n spectrum, while that at 1095 cm⁻¹ remains unchanged, but their relative absorptivities are reversed, with the band at 1160 cm⁻¹ being slightly more pronounced than that at 1095 cm⁻¹. The OH band, in the 3400-3500 cm⁻¹ region, is also modified as a broad single band in the spectrum of SiT_n , in place of a split band found in the spectrum of tartaric acid. In addition, a pronounced absorption maximum at 830 cm⁻¹, found in the SiT_n spectrum may be attributed to Si-O stretch by comparison with the IR spectra of silicon alkoxides and -acetates. The above-mentioned observations thus

suggest bonding of silicon by both the carboxylate and the secondary alcohol groups of tartaric acid.

Silicon complexes of citric and malic acids were also synthesized in THF. Both of them yielded IR spectra characteristically different from those of the free acids. The citrate complex was found to readily decompose in aqueous solution into silicic and citric acids as evidenced from titration and conductivity data. The difference in the kinetics of solvolysis of the two complexes merits further study.

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Zinc(II), cadmium(II) and mercury(II) complexes of triazene 1-oxides

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Divalent zine, cadmium and mercury ions exhibit a considerable variety in their coordination[1]. We report triazene-1-oxide[2] complexes of these metal and mixed chelates with *o*-phenanth-roline/dipyridyl.

Triazene 1-oxides (I) usually produce complexes of type (II). The triazene 1-oxides (TH) studied include the following in the order of R and Ar: CH₃, C₆H₅; CH₃, C₆H₄CH₃(m); CH₃, C₆H₄·CH₃(p); CH₃, C₆H₄·Cl(p); C₆H₅, C₆H₅; C₆H₄·CH₃(p); C₆H₅, C₆H₄·NO₂(p); C₆H₅, C₆H₄·Cl (o and p).

EXPERIMENTAL

Ligands were sythesized by published procedures [3]. The bis(ligand) metal(II) complexes were prepared as crystalline solids by reacting alcoholic solutions of the metal acetates (0.01 mole) with the ligands (0.02 mole) on a steam bath. Recrystallization were carried out from acetone. The zinc(II) and cadmium(II) complexes are stable but on refluxing for 10-15 min, the bis(ligand) mercury(II) complexes were reduced to elementary mercury to some extent. The (o-phen/dipy) bis(ligand) zinc(II) and cadmium(II) were obtained by adding o-phen/dipy in (1:1) molar ratio to the solution of bis(ligand) metal(II) complexes in acetone. The solid crystalline mixed 'chelates deposited on concentrating the solution.

Analysis. Carbon and hydrogen were determined at C.D.R.I. Lucknow (India). Nitrogen was determined using Dumas method. Zinc and cadmium were determined as oxides after igniting the complexes under A.R. oxalic acid. Mercury was estimated as sulphide.

Physical measurement. The IR spectra in the range (4000-600 cm⁻¹) were recorded at C.D.R.I., Lucknow (India). Electrical conductance measurements were made in acetone at room temperature using a Philip's conductance bridge. Molecular weights were determined in freezing benzene.

RESULTS AND DISCUSSION

Zinc(II), cadmium(II) and mercury(II) readily react with triazene 1-oxide ligands giving bis(ligand) metal(II) complexes. The analytical results of C, H, N and the metal agree with the formula $MT_2[M = Zn(II), Cd(II)$ and Hg(II)]. Conductance data in acetone $(\Lambda_M = 0-7 \ \Omega^{-1} \ cm^2 \ mole^{-1})$ show their non-electrolytic nature. Molecular weights determined in freezing benzene give monomer values within $\pm 2\%$. Selected data, conductance values and molecular weights for 7 complexes of the 45 synthesized and studied are given in Table 1. The IR spectra of all the bis(ligand) metal(II) complexes of the same triazene 1-oxide exhibit identical band positions indicating the same geometry. Since all these divalent ions have a d¹⁰ configuration it is most likely that they have tetrahedral coordination.



The formation of the mixed chelates of zinc(II) and cadmium(II) of the type $[MT_2(o-phen/dipy)]$ was confirmed by consistent analysis, conductance values, molecular weights and IR spectra, even after several recrystallizations from acetone. Unfortunately the bis(ligand) mercury(II) complexes did not yield such products. Thus, while zinc(II) and cadmium(II) give 6 coordinate mixed chelates, mercury(II) forms only 4 coordinate complexes. The non-electrolytic conductance values of the mixed chelates of zinc(II) and cadmium(II) in acetone indicate that both the triazene l-oxide ligands are still inside the coordination zone.

Table 1. Characterization data, conductance values and molecular weight of Zn(II), Cd(II) and Hg(II) complexes of TH ($\mathbf{R} = C_{\mathbf{k}}\mathbf{H}_{s}$)

Complex	Colour	M.P. (°C)	% M	% N	ЯC	% н	Λ _M	Mol.wt.
² ^T ₂	Light brown	164-65	17.48	23.08	47.75	4.89	4.8	371.8
			(17.88)*	(22.97)	(45.97)	(4.34)		(365.4)
ZnT ₂ .o-phem	Yellow	220-21	11.73	20.61	57.25	4.39	7.1	529.1
			(11,89)	(20,52)	(57.19)	(4.40)		(545.6)
ZnT ₂ -Dipy	Yellow	184-85	12.46	21.68	55.42	4.90	6.7	532.0
			(12.53)	(21.47)	(55.11)	(4.59)		(521 .6)
CaT ₂	Light brown	148-49	26.87	20.24	41.20	4.10	4.0	419.6
			(27.26)	(20.37)	(40.70)	(3.88)		(412.4)
CdT ₂ .o-phen	Yellow	192-93	18.03	18.32	53.50	4.60	4.0	586.9
			(18.77)	(18.74)	(52.66)	(4.05)		(592.6)
CdT ₂ .Dipy	Yellow	147	19.10	19.43	51.02	4.70	4.1	573.0
			(19.77)	(19.52)	(50.65)	(4.22)		(568.6)
HgT2	White	155	39,98	16.53	33.62	3.16	3.1	479.7
			(40.06)	(16.78)	(33.56)	(3.19)		(500.6)

* Values in parentheses indicate calculated ones.

IR spectra

The expected IR bands for v_{N-H} (3200 cm⁻¹), v_{C-C} (phenyl ring)(1600 cm⁻¹), $\nu_{-N=N-N}$ (sym. triazene)(1560-1450 cm⁻¹) and $\nu_{N\to O}$ (1300-1220 cm⁻¹) have all been found in the IR spectra of the triazene 1-oxide ligands [4]. The $\nu_{N\to O}$ band is found to be considerably lowered ($\sim 60 \text{ cm}^{-1}$) due to N \rightarrow O-M bond formation in the complexes[5-7]. The ν_{N-H} band of the ligand completely disappears in both MT_2 and MT_2 (o-phen/dipy) showing coordination of the metal(II) ion through the 3 N atom. But ν_{C-C} (phenyl ring) remains almost unchanged (~10 cm⁻¹). $\nu_{-N=N-N}$ is lowered by ~ 26 cm⁻¹ due to change in the environment of the triazene. The $\nu_{N\to O}$ (~1300 cm⁻¹) is lowered to (~ 1240 cm⁻¹). Both in the bis(ligand) metal(II) complex and the mixed chelates a very sharp new band at $\sim 1240 \text{ cm}^{-1}$ covers a few weak bands as well as the ν_{C-C} (phenyl in plane). Characteristic bands of coordinated o-phen/dipy (as in [Cu(dipy)Cl₂] and $[Cu(o-phen)Cl_2][8]$; $[Ni(H_2O)Cl(dipy)_2]$ Cl 2H₂O and $[Ni(H_2O)Cl(o-phen)_2]Cl 3H_2O[9]$, at 730 cm⁻¹, ~1170 cm⁻¹ and -1420 cm^{-1} appear also in the [MT₂(*o*-phen/dipy)] complexes. The IR spectra of the mixed chelates of zinc(II) and cadmium(II) containing the same ligands show identical band positions.

While some authors claim that coordination chemistry of zinc(II) and mercury(II) are closer to each other than to cadmium(II)[10] we find that zinc(II) and cadmium(II) form similar 4 coordinate as well as 6 coordinate mixed complexes but mercury(II) forms only 4 coordinate complexes. This difference may be due to the more stable s and p-orbitals of Hg(II)[11]. It may also reflect the large s-p separation (by about 2 ev) for the mercury(II) ion[12].

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Nickel(II) mixed chelates containing hydroxyaldimino amino acids and dipyridyl (or *o*-phenanthroline)

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Nickel(II) mixed ligand complexes containing a tridentate Schiff base (donor set ONN) derived from the condensation of N,N

dialkylethylenediamine and salicylaldehyde (donor set OO) were reported by Chakravorty et al.[1]. We report a number of