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Synthesis characterization and microbial activities of some bivalent metal ions complexes of 4-salicyldimino-3,5-dioxo-6-methyl-2,3,4,5tetrahydro-1,2,4-triazine

R.R.Jha¹, Rakesh Roshan^{1*}, Preethy Alex¹, Debojyoti Chakraborty², Ranvir Kumar³, L.K.Mishra³ ¹Department of Chemistry, Ranchi University, Ranchi, (INDIA) ²Department of Chemistry, NIT, Patna, (INDIA) ³Department of Chemistry, Patna University, Patna, (INDIA) E-mail : rroshan0283@gmail.com Received: 17th July, 2012 ; Accepted: 24th September, 2012

ABSTRACT

Stable complexes of bivalent metal ions with 4–salicyldimino–3,5–dioxo–6– methyl–2,3,4,5–tetrahydro–1,2,4–triazine (Hsalmtz) of composition $[M(salmtz)_2]$ (M = Co^{II}, Mn^{II}, Cu^{II}, Ni^{II}, Pd^{II}, Zn^{II}, Cd^{II}, Hg^{II} and Pt^{II}), [Cu(salmtz)X] (X = Cl⁻ or Br⁻) and [M(salmtz)X] (M = Zn^{II}, Cd^{II} or Hg^{II} and X = Cl⁻, I⁻ or NCS⁻) have been prepared analyzed and their structure have been suggested from the studies of IR, UV, magnetic susceptibility and electrical conductance measurement. The Hsalmtz and its Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II} complexes were screened for antibacterial viz. E. Coli, B. thuringiensis, S. aureus and antifungal activities on F. oxysproum, A. nigar, A. flavus and R. phaseoli. The complexes were found to be highly effective against antibacterial and antifungal species. © 2012 Trade Science Inc. - INDIA

INTRODUCTION

Triazine derivatives are highly active anti–inflammatory, anticoagulant, antiviral, antimicrobial, antibacterial and antifungal substances and a number of derivatives have been used as effective drug^[1–4]. The complexes of 4-amino-3,5-dioxo-6-methyl-2,3,4,5-tetrahydro-1,2,4-triazine (Hmtz) have been reported in previous communications^[5–7]. In view of potent pharmacological properties and stable complex forming ability of 4salicyldimino (Hsalmtz) derivatives of triazine [Hmtz] the complexes of Hsalmtz with nine bivalent biological potent metals viz Co^{II}, Mn^{II}, Cu^{II}, Ni^{II}, Pd^{II}, Zn^{II}, Cd^{II}, Hg^{II} and Pt^{II} have been prepared and characterized and antibacterial and antifungal properties of ligand and some of their compounds have also been studied and reported in present paper.

EXPERIMENTAL

Analytical grade reagents and solvents of BDH, E.Merck, Nice, and Sd. fine chemicals were used for preparation of ligand and metal complexes. Palladium (II) and Platinum (II) chloride were obtained from Johnson Matthey, London. 4-Amino-3,5-dioxo-6methyl-2,3,4,5-tetrahydro-1,2,4-triazine (A) was pre-

KEYWORDS

4-Salicyldimino-3,5dioxotriazine; Bivalent metal complexes; Characterization; Antibacterial properties. pared by known procedure^[6]. The ligand (Hsalmtz) was prepared by condensing A with equimolar proportion of salicylaldhyde in aqueous ethanol at reflux temperature in presence of 2-3 ml of acetic acid. The product was recrystallized with hot ethanol and analyzed. M.P. recorded $248^{\circ} - 250^{\circ}$ C.

Preparation of complexes $[M(salmtz)_2] (M = Co^{II}, Mn^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II})$: About 0.01 mol of metal acetate was dissolved in hot aqueous ethanol (30–40 ml) and refluxed with 0.02 mol of ligand in hot ethanol (30 ml) for half an hour and pH was raised by adding aqueous sodium acetate solution. The neutral bis chelate separated slowly. The product was digested on steam bath, cooled and collected on filter. The Pd^{II} and Pt^{II} complexes were prepared by reacting aqueous acidic solution of metal chloride with ligand in ethanol (1: 2 molar ratio) and adjusting their pH to 5–6 by adding sodium acetate solution. The yield 90–98%.

Preparation of complexes $[M(salmtz)X](X = Cl^{-}$

or Br⁻ for Cu^{II} and X = Cl⁻ or I⁻ for Zn^{II}, Cd^{II} and Hg^{II}): The ethanolic solution of metal halides (0.01 mol in 20 ml) and hot ethanolic solution of ligand (0.01 mol in 25–30 ml) were mixed together and refluxed on a steam bath with constant stirring. The halo complexes separated slowly. The products were cooled filtered and washed with ice cold ethanol (Yield 80–87%). The purity of samples was tested by TLC.

The complexes were dried in desiccator over CaCl₂. The metal contents and halogens of complexes were analyzed by standard procedure^[5–6]. The result of C, H and N were obtained on Elementar Vario EL III Carlo Erba 1108 analyzer. UV–Vis spectra were recorded at Shimadzu UV–Vis 160 spectrophotometer and FTIR were recorded in KBr disc in the range of 4000-400 cm⁻¹ on Shimadzu spectrophotometer at IIT Patna. Magnetic susceptibility was determined by Gouy method. Molar conductivities of freshly prepared solution in DMF were measured on a Systronics Conductivity TDS Meter 308. The results of elemental

TABLE 1									
Mologular formula		Elem							
of compound	Color	% of C	% of N	% of Halogen	% of M	μ _{eff.} ΒΝ 301-303 K			
$C_{11}H_{10}N_4O_3$	Cream	53.19(53.65)	22.44(22.76)			Dia			
$[Cu(C_{11}H_{10}N_4O_3)Cl]$	Ash color	38.01(38.37)	15.82(16.27)	10.0910.29)	18.14(18.45)	1.87			
$[Cu(C_{11}H_{10}N_4O_3)Br]$	Brown yellow	33.65(33.97)	14.05(14.41)	20.08(20.59)	16.03(16.34)	1.83			
$[Pd(C_{11}H_{10}N_4O_3)Cl]$	Yellow green	33.54(33.94)	14.13(14.47)		27.01(27.50)	Dia			
$[Zn(C_{11}H_{10}N_4O_3)Cl]$	White	37.89(38.16)	15.84(16.19)	10.01(10.26)	18.65(18.90)	Dia			
$[Zn(C_{11}H_{10}N_4O_3)I]$	White	29.91(30.18)	12.44(12.80)	28.89(29.03)	14.58(14.94)	Dia			
$[Zn(C_{11}H_{10}N_4O_3)NCS]$	Cream	38.69(39.09)	18.56(19.00)		17.31(17.74)	Dia			
$[Cd(C_{11}H_{10}N_4O_3)Cl]$	White	33.35(33.59)	13.86(14.25)	8.95(9.03)	28.36(28.60)	Dia			
$[Cd(C_{11}H_{10}N_4O_3)I]$	Cream	27.01(27.25)	11.19(11.56)	25.86(26.21)	22.94(23.20)	Dia			
$[Cd(C_{11}H_{10}N_4O_3)NCS]$	Cream	34.29(34.66)	16.59(16.85)		26.76(27.07)	Dia			
$[Hg(C_{11}H_{10}N_4O_3)Cl]$	White	27.21(27.43)	11.24(11.64)	7.03(7.37)	41.35(41.69)	Dia			
$[Hg(C_{11}H_{10}N_4O_3)I]$	White	22.59(23.05)	9.43(9.78)	21.98(22.17)	35.08(35.32)	Dia			
$[Hg(C_{11}H_{10}N_4O_3)NCS]$	Cream	28.52(28.59)	13.65(13.90)		39.47(39.83)	Dia			
CuL_2	Brick red	47.19(47.69)	19.94(20.23)		11.24(11.47)	1.91			
NiL ₂	Yellow	47.85(48.11)	20.09(20.41)		10.32(10.69)	3.02			
CoL_2	Reddish brown	47.65(48.09)	20.01(20.40)		10.41(10.73)	4.94			
ZnL_2	White	47.25(47.53)	19.89(20.16)		11.23(11.77)	Dia			
MnL_2	Dirty white	48.02(48.44)	20.12(20.55)		9.85(10.08)	5.92			
CdL_2	White	43.35(43.82)	18.19(18.59)		18.15(18.65)	Dia			
PdL ₂	Cream yellow	44.02(44.26)	18.45(18.77)		17.46(18.84)	Dia			
HgL ₂	White	37.98(38.22)	15.95(16.21)		17.29(18.84)	Dia			
PtL ₂	Cream yellow	38.13(38.47)	16.01(16.34)		28.09(28.47)	Dia			

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analysis of the ligand and complexes are shown in TABLE 1.

RESULTS AND DISCUSSION

The ligand 4-salicyldimino-3,5-dioxo-6-methyl– 2,3,4,5-tetrahydro-1,2,4-triazine (Hsalmtz) Figure A



can coordinate as monobasic tridentate coordinating molecule acting as (ONO) donor molecule as shown in Figure B.

The elemental analysis of bis ligated complexes correspond to formula $[M(salmtz)_{2}]$ (M = Co^{II}, Mn^{II}, Cu^{II}, Ni^{II}, Pd^{II}, Zn^{II}, Cd^{II}, Hg^{II} and Pt^{II}). These complexes are formed in weakly basic medium in presence of sodium acetate in methanolic solution. The metal halide (chloride or bromide) gave halo complexes [M(salmtz)X] (M = Cu^{II} and X = C⁻lor Br⁻) [M(salmtz)X] (M = Cd^{II}, Hg^{II} or Pd^{II} and X = Cl⁻, I⁻ and NCS⁻). The neutral bis chelates [M(salmtz)₂] have poor solubility in methanol, acetone and benzene but dissolve appreciably in DMF and DMSO, but these are almost insoluble in water. The hot aqueous suspension of halo complexes $[M(salmtz)X] (X = Cl^{-},$ Br⁻, I⁻ or NCS⁻) slowly dissociate into MX₂ and [M(salmtz)₂] yielding conducting solutions. The DMF solution of neutral bis chelates [M(salmtz),] show negligible electrical conductance values ($\lambda_{\alpha} = 6-9$ ohm⁻ ¹mol⁻¹cm²) supporting nonionic nature^[8] of [M(salmtz)₂]. The freshly prepared DMF solution of halo complexes [Cu(salmtz)X] ($X = Cl^-, Br^-$) and [M(salmtz)X] (M = Zn^{II}, Cd^{II}, Hg^{II}, Pd^{II} or Pt^{II} and X =

Cl⁻, I⁻ and NCS⁻) show negligible electrical conductance value($\lambda_{\alpha} = 6 - 10 \text{ ohm}^{-1} \text{mol}^{-1} \text{cm}^2$) suggesting halides (Cl⁻, Br⁻, I⁻ or NCS⁻) to be coordinated in halo complexes. The DMF solution of halo complexes on long standing display appreciable electrical conductance value($\lambda_{q} = 60 - 100 \text{ ohm}^{-1} \text{mol}^{-1} \text{cm}^{2}$) suggesting solvolysis of complexes liberating anion from coordination sphere. The magnetic susceptibility (301⁰-303ºK) of Pd^{II}, Zn^{II}, Cd^{II}, Hg^{II} or Pt^{II} complexes $[M(salmtz)_{2}]$ and [M(salmtz)X] (M = Pd^{II}, Zn^{II}, Cd^{II} or Hg^{II} and $X = Cl^{-}$, I^{-} , or NCS⁻) were found to be diamagnetic as expected for these complexes. The Cu^{II}, Co^{II}, Ni^{II} and Mn^{II} complexes are paramagnetic. The effective magnetic moment of [Co(salmtz),] is 4.94 BM and that of [Ni(salmtz),] is 3.02 BM suggested octahedral environment of ligands around Co^{II} and Ni^{II}. The μ_{eff} = 5.92 BM for [Mn(salmtz)₂] and its dull white color are similar to octahedral Mn^{II} complexes^[9]. The magnetic moment value of Cu^{II} complexes $[Cu(salmtz)_{2}]$ and [Cu(salmtz)X] (X = Cl⁻ or Br⁻) occur between 1.83-1.91 BM usually observed for magnetically dilute Cu^{II} complexes having distorted octahedral geometry^[9]. The electronic absorption spectral studies of ligand and its complexes in ethanol display some prominent absorption band characteristic for ligand molecule functional group and geometry of metal complexes. The ligand display three strong electronic absorption band located at 218, 245 and 287 nm and medium band at 323 nm. The electronic absorption band of Hsalmtz is assigned as $\sigma \rightarrow \sigma^*, \pi \rightarrow \pi^*$ (ring C=N and aldimine group) $\pi \rightarrow \pi^*$ (C=O) and $n \rightarrow \pi^*$ transition of triazine and salicyldimino substituent. In transition metal complexes salcyldimino group (C=N) nitrogen, one of the oxo (C=O) oxygen and deprotonated phenolic oxygen are expected to be involved in bonding and thus these transition have been observed at lower energy or get eclipsed in charge transfer $L \rightarrow M$ or $M \rightarrow L$ strong absorptions. The electronic absorption spectrum of Co^{II} complex [Co(salmtz)₂] display strong absorption below 380 nm in DMF and ethanol. The complex show medium shoulders at 440 and 530 nm. These bands are assigned to ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}(P)$ and ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$ transitions in distorted octahedral field around Co^{II} atom^[10].

In case of Zn^{II}, Cd^{II} and Hg^{II} complexes no d–d transitions are expected but electronic transitions due

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to metal – ligand interaction observed as $n \rightarrow \pi^*$ transition and merge with ligand absorption. The Zn^{II}, Cd^{II} and Hg^{II} complexes in dilute DMF solution display electronic absorption bands at 215-222, 245-260, 282–292 and 330–342 cm⁻¹ due to $\sigma \rightarrow \sigma^*, \pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions for coordinated ligand molecule. The Mn^{II} complex $[Mn(salmtz)_2]$ do not display distinct spectral transition similar to octahedral Mn^{II} complexes^[10] due to spin forbidden nature of absorption bands. The Pd^{II} and Pt^{II} complexes [M(salmtz)₂] display strong absorption below 390-400 nm and a should r near 400–410 nm attributed to ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ transition in planer field. The Cu^{II} bis chelate display broad asymmetric band at 540 nm attributed to ${}^{2}E_{a}$ $\rightarrow {}^{2}T_{2\alpha}$ transition for distorted structure. The chloro and bromo complexes [Cu(salmtz)X] display broad band between 650–710 nm assigned as ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ $+{}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transitions^[10-12]. The greenish yellow Ni^{II} bis chelate [Ni(salmtz)₂] display two medium to weak band located at 410 nm as shoulder and medium band near 620 nm. These bands are broad and assigned as ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}(F)$ and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$ transitions in octahedral field.

The IR spectrum of Hsalmtz display a broad band at 3180–3340 cm⁻¹ attributed from hydrogen bonded v(OH) of phenolic group and this broad vibration is absent in almost all complexes $[M(salmtz)_2]$ and [M(salmtz)X] supporting the deprotonation of phenolic OH and bonding through deprotonated phenolic oxygen^[13–16]. The sharp infrared band at 2941 and 2883 cm⁻¹ can be attributed to (C–H) stretch of – CH₃ group. The triazole ring (N–H) stretch of ligand

displays a medium band at 3130 ± 15 cm⁻¹ which is retained in almost all complexes but observed as broad band due to hydrogen bonding[15-16]. The IR stretching band of oxo group (C=O) were observed at 1720 cm⁻¹ as strong and medium band at 1660 cm⁻¹. The former v(CO) of ligand is shifted to lower frequency by 40–60 cm⁻¹ and observed as strong and broad band near 1663 ± 10 cm⁻¹ in both neutral bis chealate $[M(salmtz)_{2}]$ (Co^{II}, Cu^{II} and Ni^{II}) and [M(salmtz)X] $(M = Cu^{II}, Cd^{II} \text{ or } Hg^{II} \text{ and } X = Cl^{-}, Br^{-} \text{ or } NCS^{-}).$ The blue shift of v(C=O) stretch in complexes supports the involvement of ring carboxo (CO) oxygen in coordination is above all metal complexes^[17-20]. In case of complexes $[M(salmtz)_2]$ $(M = Pd^{II}, Pt^{II}, Zn^{II})$ and Cd^{II}), v(CO) is not affected appreciably showing that CO oxygen are not involved in bonding and ligand is bidentate. The v(C=N) of triazine ring is absorbed at 1595 cm⁻¹ as medium band and is not affected appreciably in complexes suggesting that it is not involved in bonding in metal complexes. The phenolic v(CO)of salicyldimino group can be assigned to a medium band at 1170 cm⁻¹ in ligand and its shift on deprotonation in complexes around 1305 ± 15 cm⁻¹ indicated that bond order of phenolic v(C-O) group is enhanced on coordination with deprotonated phenolic oxygen. The strong and sharp band at 2115 and 715 wave number in [Hg(salmtz)(SCN)] is attributed v(C=N) and v(C=S) of S coordinated thiocyanato group but in case of [Zn(salmtz)(NCS)] and [Pd(salmtz)(NCS)] the broad and strong band at 2085 and 2090 cm⁻¹ and medium band at 816 and 795 cm⁻ ¹ is assigned to N coordinated thiocyanato group re-

Compound	v(OH) phenolic	v(CO)	v(CN)	v(CO)	v(NN)	v(MO)	v(MN)
Hsalmtz	3280–3340 3160 v(NH)	1720(s) 1660(s.br.)	1595(st.)	1170(m)	1215(m)	568(m)	422(w)
[Co(salmtz) ₂]	3145	1665(s.br.)	1592(st.)	1305(m)	1210(m)	515(m)	430(w)
[Cu(salmtz) ₂]	3138	1670(s.br.)	1590(st.)	1302(m)	1212(m)	520(m)	435(w)
[Ni(salmtz) ₂]	3140	1655(s.br.)	1595(st.)	1306(m)	1215(m)	515(m)	418(w)
$[Zn(salmtz)_2]$	3130	1715(s)	1590(st.)	1320(m)	1211(m)	522(m)	408(w)
[Cd(salmtz) ₂]	3120	1710(s)	1592(st.)	1325(m)	1208(m)	512(m)	413(w)
[Pd(salmtz) ₂]	3125	1712(s)	1595(st.)	1320(m)	1207(m)	518(m)	418(w)
[Cd(salmtz)Cl]	3125	1670(s.br.)	1592(m)	1325(m)	1210(m)	522(m)	413(w)
[Cu(salmtz)Cl]	3130	1668(s.br.)	1592(m)	1320(m)	1212(m)	516(m)	421(w)
[Cu(salmtz)Br]	3135	1672(s.br.)	1596(st.)	1312(m)	1215(m)	520(m)	408(w)
[Cd(salmtz)I]	3142	1672(s.br.)	1595(st.)	1325(m)	1205(m)	518(m)	421(w)

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spectively^[13,19].

The ligand and its complexes display a number of medium and strong IR bands due to phenyl ring skeletal vibrations v(C=C), v(N=N), v(C–N), δ (NH), v(C–C), and δ (CH) of phenyl and methyl group and are located at 1545, 1505, 1465, 1384, 1321, 1213, 1170, 1015, 912, 812, 745, 650 and 568 cm⁻¹. These vibrations are not affected predominantly in complexes. The new IR bands observed in the range 500–525 cm⁻¹ are assigned to (M–O) and IR bands in the range 408–435 cm⁻¹ are assigned (M–N) vibrations^[15,18]TABLE 2.

ANTIBACTERIALAND ANTIFUNGAL ACTIVITY

The antifungal activity of the ligand and its complexes have been evaluated by radial growth method^[21] Czapek agar medium prepared by dissolving 20g starch, 20g agar agar and 20g glucose in one liter distilled water. The resulting medium was added requisite amount of test compound to get 50, 100 and 200 ppm of solution. The medium was then poured into Petri plates and the spores of fungi were placed on medium with the help of inoculum needle. These Petri plates were wraped in polythene bags containing two to three drops of ethanol and then placed in an incubator at $30 \pm 0.5^{\circ}$ C. The linear growth of fungus was evaluated by measuring the fungal colony diameter after five day. The percentage

inhibition was calculated from the relation $\frac{100 (C-T)}{C}$ where

C and T are the diameter of the fungus colony and control test plates respectively. The fungi used in present investigation included F. oxysporum, A. niger, A. flavus and R. phaseoli. The control solution was mycostalin. The result of activity is shown in TABLE 3. The results show that antifungal activities of complexes are larger than free ligand. The activity increases with increasing concentration of the substances from 50<100<200 ppm. The greater fungal activity may be due to large electron cloud delocalization which increases lipophilic nature of the central metal atom causing permeation through the lipid layer of cell membrane. The activity against bacteria E. coli, B. thuringiensis and S. aureus were evaluated by inhibition zone technique^[22]. The nutrient agar medium was prepared taking 5g peptone; beef extract 5g, NaCl

TABLE 3 : Antimicrobial activity of Hsalmtz and its complexes. Antifungus inhibition after 120 hrs and antibacterialinhibition after 24 hrs

Fungi or bacteria	Conc ⁿ	HL	NiL ₂	CuL ₂	ZnL ₂	CdL ₂	HgL ₂	Cu(LH)Cl	CoL ₂	Cd(HL)I	Ref
F.oxysporum	50	38	43	44	42	43	42	45	40	39	70
	100	47	52	56	52	55	54	53	51	50	86
	200	65	72	75	70	71	73	71	68	67	98
A.nigar	50	35	38	41	40	38	40	41	42	39	72
	100	43	46	50	50	47	46	47	48	46	83
	200	61	66	68	68	67	68	69	68	66	97
A.flavus	50	63	40	41	42	43	41	42	39	41	71
	100	42	46	47	48	54	50	52	43	48	91
	200	61	65	67	68	70	65	68	62	63	100
R.phaseoli	50	43	45	46	42	44	43	42	41	43	70
	100	52	55	55	53	56	54	52	53	53	85
	200	63	71	70	67	65	63	69	68	69	100
Antibacterial inhibition											
E.Coli	250	11	12	10	13	12	10	11	12	12	1
	500	15	16	14	16	17	15	14	15	16	2
B.thuringiensis	250	11	13	11	11	11	11	11	12	13	2
	500	14	17	15	14	16	14	15	16	16	3
S.aureus	250	13	15	12	12	12	12	12	12	11	3
	500	15	16	15	16	16	15	16	16	14	5

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5g, and agar agar 20g in one liter distilled water. The solution was pipeted into Petri plate dried and added seeded agar with bacteria. The compound was dissolved in DMF having 250 and 500 ppm strength. The discs of Whatman no. 1 filter paper soaked with these solutions to 5 mm diameter discs were dried and placed on the medium previously seeded with organism in Petri plate at suitable distance. The Petri plates were stored in an incubator at $30 \pm 1^{\circ}$ C for twenty four hours. The zone of inhibition was measured accurately in millimeter. The results are shown in TABLE 3. It is found that metal complexes show higher activity than free ligand.



CONCLUSION

The ligand coordinates as tridentate anionic molecule as (ONO) donor but as bivalent (NO) donor in neutral bis chelate $[M(salmtz)_2]$ (M = Pd^{II}, Pt^{II}, Zn^{II}, Cd^{II} and Hg^{II}).

D

From the results of physical and analytical analysis the probable structure of complexes are shown in Figure C, D and E

The probable structure of bis chelate $[M(salmtz)_2]$ (M = Co^{II}, Ni^{II}, Cu^{II} and Mn^{II}. Figure C). $[M(salmtz)_2]$ (M = Cd^{II}, Zn^{II}, Hg^{II} or Pd^{II}. Figure D), [M(salmtz)X](M = Cu^{II}, Cd^{II} Figure E).

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