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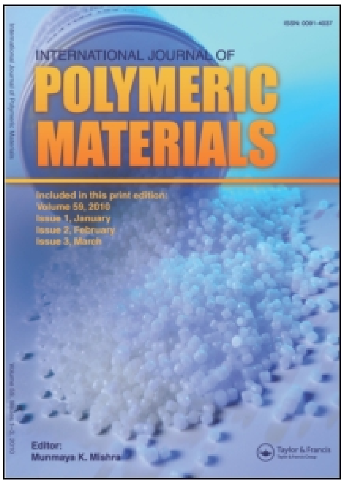

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Polychelates Derived from 4,4' -(4,4'-Biphenylylene bisazo) di (Resacetophenone)

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Polychelates Derived from 4,4′-(4,4′-Biphenylylene bisazo) di(Resacetophenone)

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Polychelates of Ni(II), Co(II), Zn(II), Cu(II) and Mn(II) were synthesized from bis 4,4′-(4,4′-biphenylylenebisazo) di (resacetophenone) and metal chlorides. All these chelates are dark in colour and insoluble in common organic solvents. Their most probable structures were determined by visible reflectance spectroscopy and magnetic measurements in conjuction with thermogravimetric and IR measurements. Elemental analyses indicate a ligand: metal ratio of 1:1 and association of water molecules with the central metal. The decomposition of temperatures of the polychelates decrease in the following order: Zn(II) > Co(II) > Ni(II) > Mn(II) > Cu(II).

Keywords: Polychelates; 4,4′-(4,4′-biphenylylenebisazo)di(resacetophenone); metal chlorides

INTRODUCTION

There are many reports about the Co-ordination (*i.e.*, Chelate) polymers derived from bis ligands [1–3] Shah *et al.* [4–6] reported a number of such chelate polymers. One of the ligand resacetophenone [7] made from 4,4′-(4,4′-biphenylylenebisazo)-di-resacetophenone and may yield co-ordinations polymers. The introduction of – azo group into the co-ordination polymer may enhance the properties like thermal, semi conductivity and pigmentating. Hence it was thought

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*Corresponding author.

interesting to study the co-ordination polymers based on bis ligand containing resacetophenone. This paper reports on the preparation and properteis of chelate polymers of the bisoxime of 4,4′-(4,4′-biphenylylenebisazo) di (resacetophenone) with Cu(II), Ni(II), Co(II), Mn(II) and Zn(II).

EXPERIMENTAL

Materials

Resacetophenone (from British Drug House) was used after distillation: Benzidine (from SD's Laboratory Chemical Industries) was used after purification. Metal chlorides (from British Drug House) were applied for the preparation of polychelates. *N*, *N*′-dimethylformamide (DMF, from Sarabhai M. Chemicals) was used without further purification. All other chemical used were of AnalaR grade.

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Preparation of Ligand

A cold tetraazotized solution of benzidine (0.05 mol.) was poured into a cold solution of resacetophenone (0.053 mol.) and Na_2Co_3 (23 g) in water (100 ml) and the mixture was stirred for 3–4 hr. When the coupling of one mole of resacetophenone was complete, a second mole resacetophenone (0.053 mol.) dissolved in a minimum quantity of NaOH solution was added and stirring was continued untill the reaction was complete. The precipitated 4,4′-(4,4′-Biphenylylenebisazo) di resacetophenone was filtered off, washed and dried yield: 69%. Its bisoxime, 4,4′-(4,4′-Biphenylylenebisazo) di(resacetophenone oxime), was prepared by the aqueous DMF alkali method [8].

Preparation of Complexes

The ligand (0.01 mol) was dissolved and refluxed in 100 ml of DMF. To the refluxed ligand solution, the metal chloride solution (0.01 mol. in 20 ml water) was added slowly with constant stirring. To the resulting mixture, 0.5 g of sodium acetate was added and heated in an oil both at 130°C for 4 hr. The brown precipitated solid (0.008 mol, 80% yield) was filtered off and washed several times with hot water, hot DMF and finally with ethanol and dried at 80°C.

Properties

All the chelate polymers are dark coloured solids and insoluble in common organic solvents. It was not possible to characterized them by conventional methods, like osmometry; viscometry *etc.*, as they are insoluble. All of them are thermally stable (See Tab. II).

COMPOSITION

The metal composition of each polymer was determined by independent gravimetric and volumetric methods. In gravimetric method, about 1.0 g of the compound was accurately weighed in a crucible and decomposed simply by heating it carefully, first gently (~250°C) for about 3 hr until constant weight is obtained. The residue was weighed as oxide (NiO, CoO, CuO, ZnO and MnO). On the other in the volumetric method an EDTA titration method was used. In this method an accurately weighed amount of chelate polymer was taken in 250 ml beaker, moistened with a concentrated sulphuric acid and nitric acid and heated on a sand-bath in a fuming chamber till all the fumes are evolved. The cooled contents were carefully transferred into a 50 ml measuring flask using double distilled water. The Ni(II) and Cu(II) EDTA titration were carried out using a buffer (pH 10) and murexide as indicator and the Co(II) EDTA titration using xylenol orange as indicator and hexamine powder at 50°C. The Mn(II) and Zn(II) EDTA titration carried out using a buffer (pH10) and Eriochrome black-T as indicator. In the case of Mn(II), ascorbic acid powder was used additionally, 0.01 ml EDTA was used as titrating solution. Carbon and Hydrogen contents were determined by the usual microanalytical methods. The results of elemental analysis are given in Table I.

Spectral Studies

All physiochemical measurement were carried out at room temperature. The IR spectra (See Tab. V) were recorded in KBr on a

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TABLE I Analytical results of the polychelates

Compounds	*Molecular weight*		*Elemental analysis*			*Electrical Conductivity*
			C	*H*	*N*	$\Omega\ cm^{-1}$
$[Cu(C_{27}H_{18}N_6O_5)3H_2O]_n$	625.54	Found	51.20	3.50	13.10	8.9×10^{-10}
		Calc.	51.84	3.84	13.44	8.9×10^{-10}
$[Ni(C_{27}H_{18}N_6O_5)(H_2O)_2H_2O]_n$	620.21	Found	52.10	3.60	13.20	7.3×10^{-10}
		Calc.	52.25	3.87	13.54	7.3×10^{10}
$[Co(C_{27}H_{18}N_6O_5)(H_2O)_2 2H_2O]_n$	620.93	Found	52.20	3.90	13.20	4.0×10^{-11}
		Calc.	52.25	4.19	13.54	4.0×10^{-11}
$[Mn(C_{27}H_{18}N_6O_5)(H_2O)_2H_2O]_n$	616.93	Found	51.90	3.70	13.40	12.0×10^{-9}
		Calc.	52.59	3.89	13.63	12.0×10^{-9}
$[Zn(C_{27}H_{18}N_6O_5)(H_2O)_2]_n$	609.38	Found	52.70	3.30		6.9×10^{-11}
		Calc.	53.20	3.61	13.79	6.9×10^{-11}

TABLE II TG data of the polychelates

Temp in °C	*Weight loss of ligand in %*	*Percentage of weight loss of*				
		Mn	*Co*	*Ni*	*Cu*	*Zn*
100	2.2	5.1	9.3	5.2	6.7	3.7
150	4.1	7.2	12.4	7.3	8.6	5.1
200	5.9	10.5	14.2	9.6	9.5	5.7
250	7.6	11.0	15.4	10.2	11.5	6.4
300	9.5	12.5	17.3	10.4	14.8	7.7
350	11.7	37.8	18.6	11.5	16.6	9.2
400	14.6	57.1	30.2	27.8	18.4	11.6
500	22.0	66.8	72.5	81.6	25.2	73.4
600	27.5	68.5	75.7	82.4	30.0	81.6
700	32.4	68.8	76.3	83.3	35.0	82.2

Spektronom-2000 spectrophotometer. The visible reflectance spectra (Tab. III) were taken on a Backman DU Spectrophotometer.

Magnetic Measurements

Magnetic susceptibility (Tab. III) were measured on a standard Gouy balance using $Hg[Co(NCS)_4]$ as calibrant.

Thermogravimetry

The thermogravimetry results were recorded on a 'Dupont' analyzer with a heating rate of 10°C/min. The weight loss (in %) at different temperatures is given in Table II.

TABLE III Decomposition temperature, magnetic moment and electric spectral data of the polychelates

Compound	*Decomposition temp in °C*	*Magnetic moment in B.M*[a]	*Transition in cm^{-1}*
$[(C_{27}H_{18}N_6O_5)H_2O]$	360	–	–
$[Cu(C_{27}H_{18}N_6O_5)\ 3H_2O]_n$	280	1.82	14295, 21060, 25000
$[Ni(C_{27}H_{18}N_6O_5)\ (H_2O)_2\ H_2O]_n$	410	2.80	9090, 15370 21060
$[Co(C_{27}H_{18}N_6O_5)\ (H_2O)\ 2H_2O]_n$	415	5.21	10000, 18860, 15390, 22980
$[Mn(C_{27}H_{18}N_6O_5)\ (H_2O)_2H_2O]_n$	340	5.57	19020, 22230
$[Zn(C_{27}H_{18}N_6O_5)\ (H_2O)_2]_n$	440	Diamagnetic	–

[a] 1 Bour magneton = $9.274078 \cdot 10^{-24}$ J.T^{-1}·.

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TABLE IV Electronic spectral data and calculated transition energies in cm^{-1} of the spin allowed bands in Ni(II) and Co(II) polychelates

Compound	*Method of calculation of B*	*Transitions* ϑ_1	ϑ_2	ϑ_3	B_{35}	B_{35} [a]	∂_{ν} [b]	$10Dq$	ϑ_2/ϑ_1
		1	2	3					
$[Ni(C_{27}H_{18}N_6O_5)(H_2O)_2(H_2O)]_n$	Expt.	9090	15370	21040	–	–	–	–	1.67
	(a)	$10Dq$	fitted	10847	605	0.560	−1189	–	
	(b)	$10Dq$	13825	fitted	662	0.611	−1543		
	(c)	$10Dq$	15211	21210	509	0.471	± 161		
	(d)	$10Dq$	13817	22605	540	0.493	± 1552		
$[Co(C_{27}H_{18}N_6O_5)(H_2O)_2 2H_2O]_n$	Expt.	10000	18860	22990	–	–	–	–	1.87
	(a)	fitted	17693	fitted	824	0.729	−1171	9414	
	(b)	8641	fitted	fitted	995	0.892	−1358	9897	
	(c)	7800	16865	fitted	789	0.705	−2200	8873	

[a] $\beta_{35} = B_{35}$ complex$/B_{\text{freeion}}$; [b] $\partial_{\vartheta} = \vartheta_{\text{calc}} - \vartheta_{\text{expt}}$.

TABLE V IR spectral data, wave numbers in cm^{-1} [a]

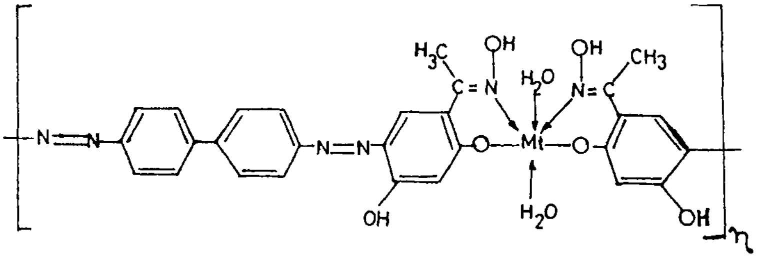
Ligand	Cu	Ni	Co	Mn	Zn
3040 vs, vbr	3250 m, br	3300 m, br	3200 vs, vbr	3250 vs, vbr	3300 vs, vbr
1620 w, s	1620 w, s	1620 w, s	1620 w, s	1620 w, s	1620 w, s
1585 vs, vs	1580 vs, s	1570 vs, s	1600 vs, s	1582 vs, s	1580 vs, s
1385 m, s	–	–	–	–	–
1305 s, br	1320 s, br	1300 vs, s	1310 vs, br	1300 w, s	1305 v, s

[a] vs = very strong; vbr = very broad; w, s = weak, sharp; m, s = medium, sharp; sh = shoulder.

The electrical conductivity of these polychelates has also been measured at room temperature following the method reported [8]. The data are given in Table I.

RESULTS AND DISCUSSION

The element analyses (Tab. I) suggest 1:1 (metal: ligand) stoichiometry for the chelate polymers. They also suggest the possibility of the association of water. The following general Structure 1 may be given for the chelate polymers.



(Mt = Mn, Co, Ni, Zn, Cu)

This type of association of water in chelate ploymers has already been observed in our laboratory [4], with a similar bioxime type ligand and several of such reports can be found in the literature [9–11]. This seems to be reasonable since water allows to reach the max. coordination number of the metal ion of six.

From the TG curves (not shown) (Tab. II) it was observed that the ligand lose 4.2% of weight at 150°C, which may be attributed to the

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pressure of one molecule of water as ligand in the molecule. The weight loss of the Cu(II), Ni(II), and Mn(II) polychelates correspond to three molecules of water per repeating unit of polychelate. Co(II) and Zn(II) chelates show weight losses corresponding to 4 and 2 molecules of water per molecule of chelate, respectively. The decomposition temperatures of the polychelates decreasing in the following order Zn(II) (430°C) > Co(II) (405°C) > Ni(II) (400°C) > Mn(II) (330°C) > Cu(II) (270°C). The Cu(II) and Mn(II) chelates are found to be thermally less stable then even the ligand. No sharp weight loss is observed with the Ni(II), Co(II) and Mn(II) polychelates indicating that the behaviour of water molecules is different in these polychelates.

Considering the thermal data along with other properties, the formulae in Table I were derived.

The visible reflectance spectrum (Tab. III) of the Cu(II) polychelate shows three bands at 14290, 21050 and 2500 cm^{-1}, which may be assigned to the square planar streochemistry of the chelate polymer [12]. The first two bands may be assigned to the $^2A_{2g} \longleftarrow {}^2B_{2g}$ and $^2E_g \longleftarrow {}^2B_{2g}$ transitions, respectively. The third one may be of charge transfer in origin. Jorgensen [13] has used the ratio $\vartheta_{Cu}/\vartheta_{Ni}$ of the wave number of the principal band of a Cu(II) complex to the first spin-allowe band of the high-spin octahydral Ni(II) complex with the same ligand, as a measure of the tetragonality of the Cu(II) complexes. The ratio of 1.58 obtained suggests high tetragonal distortion. The observed magnetic moment is very close to the spin-only value.

In case of Ni(II) polychelate the *d-d* transitions at (ϑ_1) 15380 cm^{-1}; 9090 cm^{-1} (ϑ_2) and 21050 (cm^{-1}) (ϑ_3) may be assigned to $^3T_{2g}(F) \longleftarrow {}^3A_{2g}(F)$, $^3T_{1g}(F) \longleftarrow {}^3A_{2g}(F)$ and $^3T_{1g}(P) \longleftarrow {}^3A_{2g}(F)$ transitions, respectively, characteristic of octahedral stereochemistry [14]. These ratio ϑ_2/ϑ_1(1.69) lies in the range required for Ni(II) octohydral complexes.

To compute the important ligand field parameters we have used ligand field theory of spin allowed transitions [15]. The transition energies can be obtained from the following equations.

$$E(^3A_{2g}) = -12Dq$$

$$E(^3A_{2g}) = 2Dq$$

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Dq is a radial parameter (determined emperically from spectra) defined as

$$Dq = (1/6)(Ze^2 r^{-4}/a^5)$$

where Ze = charge on ligand, r^{-4} = mean fourth power radius of d-electrons, and a = distance of the ligand point charge from the central metal ion.

The two $^3T_{1g}$ states are mixing by term interaction and their energies have to be determined from the following secular determinant.

$$\begin{array}{c|cc|}
 & T_{1g}(F) & T_{1g}(P) \\
T_{1g}(F) & 6Dq - E & 4Dq \\
T_{1g}(P) & 4Dq & 16B - E
\end{array} = 0$$

Which results in

$$E_{1,2}(^3T_{1g}) = 7.5B + 3Dq \pm 1/2[(225B^2 + 100D_q^2 - 180DqB]^{1/2}$$

These equations lead to:

$$\vartheta_1 = 10Dq$$
$$\vartheta_2 = 1/2(15B + 30Dq) - 1/2[(15B - 10Dq)^2 + 120DqB)^{1/2}]$$

The following equations were used to calculate B. The racah electron repulsion parameter.

a) $$B = \frac{(2\vartheta_1^2 + \vartheta_2^2 - 3\vartheta_1\vartheta_2)}{(15\vartheta_2 - 27\vartheta_1)}$$

b) $$B = \frac{(\vartheta_1^2 + \vartheta_3^2 - 3\vartheta_1\vartheta_3)}{(15\vartheta_3 - 27\vartheta_1)}$$

c) $$B = \frac{(\vartheta_2 + \vartheta_3 - 3\vartheta_1)}{15}$$

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d) $$B = \frac{1}{75}[3\vartheta_1 + \{25(\vartheta_3 - \vartheta_2)^2 - 16\vartheta_1^2\}^{1/2}]$$

These results are given in Table IV. Among the different procedures used for band fitting the best fit as observed by method (*C*). B_{35} is found to be considerably smaller when compared to the free ion value (1080 cm^{-1}) which indicates an appreciable amount of covalent character in the bands. An attempt has been made to obtain an approximate value of (spinorbit coupling λ) using [16],

$$\lambda_{\text{calc}} = \frac{2.7B_{35}^2}{10\,Dq\,B_{35}\,(506\,\text{cm}^{-1})}$$

was used as obtained by method (*C*), λ_{calc} was found to be 76 cm^{-1}, which much lower than the free in value. The magnetic moment of the polychelate is in the range required for an octahedral structure. To correlate the spectral and magnetic properties, ω_{eff} was calculated by

$$\mu_{\text{eff.}}^{\text{calc.}} = \mu_{\text{eff.}}^{\text{s.o}}[1 - 4\lambda_{\text{calc.}}|10Dq] \qquad [17]$$

The calculated value (2.92) is found to be a little higher than the experimental value indicating good correlation between experimental spectral and magnetic properties.

The reflectance spectra of the Co(II) polychelate shows two regions of absorption one around 10000 cm^{-1} and another at 22990 cm^{-1}. There are two shoulders at 15370 and 18860 cm^{-1}. The most probably assignment for the Co(II) octahedral chelate can be given as;

$$\begin{array}{lll} {}^4T_{2g}(F)\longleftarrow{}^4T_{1g}(F) & \vartheta_1 & 10000\,\text{cm}^{-1} \\ {}^4A_{2g}(F)\longleftarrow{}^4T_{1g}(F) & \vartheta_2 & 18860\,\text{cm}^{-1} \\ {}^4T_{1g}(P)\longleftarrow{}^4T_{1g}(F) & \vartheta_3 & 22990\,\text{cm}^{-1} \end{array}$$

The lower energy shoulder might be due to a spin-forbidden transition.

These transition energies have been used to obtain the important ligand field parameters [15]. According to the weak field approximation the energies of the transitions can be obtained from the following equations.

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$$E({}^4\mathrm{T}_{2g})(\mathrm{F}) = 2Dq$$
$$E({}^4\mathrm{A}_{2g})(\mathrm{F}) = 12Dq$$

The two ${}^4\mathrm{T}_{1g}$ states are mixed by the interaction term and their energies have to be determined from:

$$\begin{array}{c|cc|c} & {}^4\mathrm{T}_{1g}(\mathrm{F}) & {}^4\mathrm{T}_{1g}(\mathrm{P}) & \\ {}^4\mathrm{T}_{1g}(\mathrm{F}) & -6Dq - E & 4Dq & = 0 \\ {}^4\mathrm{T}_{1g}(\mathrm{P}) & 4Dq & 15Dq - E & \end{array}$$

Which results in

$$E_{1,2}({}^4\mathrm{T}_{1g}) = 7.5B - 3Dq \pm 1/2(225B^2 + 100D^2q + 180Dq \cdot B)^{1/2}$$

These equations lead to

$$\vartheta_1 = 1/2(10Dq - 15B) + 1/2[(10Dq + 15B)^2 - 120Dq \cdot B]^{1/2}$$
$$\vartheta_2 = 1/2(30Dq - 15B) + 1/2[(10Dq + 15B)^2 - 120Dq \cdot B]^{1/2}$$
$$\vartheta_3 = [(10Dq + 15B)^2 - 120Dq \cdot B]^{1/2}$$

The following equations were used to calculate $10Dq$ and B.

a)
$$10Dq = 2\vartheta_1 - \vartheta_3 + 15B$$
$$B = 1/30[-(2\vartheta_1 - \vartheta_3) \pm \{\vartheta_1^2 + \vartheta_3^2 + \vartheta_1\vartheta_3\}^{1/2}]$$

b)
$$10Dq = 1/3(2\vartheta_2 - \vartheta_3) + 5B$$
$$B = \frac{1}{510}[7(\vartheta_3 - 2\vartheta_2) + 3\{81\vartheta_3^2 - 16\vartheta_2(\vartheta_2 - \vartheta_3)\}^{1/2}]$$

c)
$$10Dq = \vartheta_2 - \vartheta_1$$
$$B = (\vartheta_2 + \vartheta_3 - 3\vartheta_1)/15$$

The results are also given in the Table IV. The ϑ_2/ϑ_1 ratio (1.88) comes very close to the ratio required for an octahedral structure [18].

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The Magnetic moment is in the range 4.7 to 5.2 B.M. required for high-spin octahedral stereochemistry.

The spectram of the Mn(II) polychelate shows two bands at 19020 and 22230 cm^{-1} which may be assigned to $^4T_{1g}(G) \longleftarrow {}^6A_{2g}$ and $^4T_{2g}(G) \longleftarrow {}^6A_{2g}$, respectively, indicating an octahedral structure for the polychelate [19]. The observed moment is lower than the spin only value (5.92 B.M.), suggesting the presence of a metal–metal interation [2].

Zn(II) polychelate is diamagnetic and may have an octahedral structure.

Important IR spectral data are given in Table V. All compounds contain four aromatic systems, hence the region characteristics of double bond is comprised of several bands which overlap with each other. This makes an interpretation of the C=C stretching region complicated. Even the out-of-plane bending region is diffiicult to interpret. It is not possible to assign the bands due to C=N bonds as they can be confused with the bands due to N=N bonds. Some important observations are indicating below.

i) The ligand as well as the polychelates show a strong and broad absorption in the range of 3050–3300 cm^{-1} which may be due to a coupling of the stretching vibrations of water, the phenolic group and the hydroxy imino hydroxyl group.
ii) The strong band at 1580 cm^{-1} with a weak band of shoulder at about 1620 cm^{-1} might be due to C=N and N=N bands.
iii) The bands at 1380 cm^{-1} might be caused by deformation vibrations of phenolic hydroxyl groups. This band is absent in the polychelates, indicating the dissociation of the phenolic proton or coordination.
iv) The ligand as well as the polychelates show strong and broad bands at 1300 cm^{-1} which may be assigned to phenolic C—O vibration. On chelation this band does not show a marked shift, indicating that this frequency is not sensitive to chelation [20]. The insolubility of polychelates in common organic solvant and their thermal stability support their polymeric structure.

The polymeric chain may be straight, formed by the participation of Phenolic 'O' and 'N' of the hydroxyimino group. The octahedral

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geometry of the complexes accounts for the association of two water molecules with a metal ion. In the case of the Cu(II) polychelate, association of water molecules may not be present.

The results of electrical conductivity of these polymers reveals that they can be ranked as semi-conductors at room temperature.

Further results obtained with more such symmetric tetrafunctional ligands will be reported soon.

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