

## Systematics of metal–ligand binding energies

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**Abstract** - An important aspect in the thermochemistry of coordination complexes is the binding energies of ligands to metals. Although bond-energy schemes are successful for alkanes and substituted alkanes they are not easily applied to coordination compounds. Dissociation energies are not a direct measure of binding energies because of the reorganization energies of the radicals. A more profitable approach is to consider the dissociation energy of the complex relative to that of the ligand with hydrogen. In normal circumstances,  $\overline{DH}(M-L) - DH(H-L)$  for a particular metal and type of ligand appears to be constant. This leads to simple relations between enthalpies of formation of complexes and their corresponding ligands which are useful for evaluating existing data and for predicting unknown enthalpies of formation.

### INTRODUCTION

Thermochemical data can be interpreted in various ways depending on the purposes for which these data are required. Metal-ligand binding energies can in principle, be considered in the context of bond-energy schemes or in terms of bond dissociation energies and the applicability and value of these approaches are quite different.

### BOND ENTHALPIES

The enthalpy of atomization of a molecule can be apportioned amongst the bonds of the molecule so that,

$$\begin{aligned} \Delta_a H^\circ &= \Sigma \Delta_f H^\circ(\text{atoms, ground state, g}) - \Delta_f H^\circ(\text{compound, g}) \\ &= \Sigma \text{Bond enthalpies} + \text{Stabilization energy} - \text{Strain energy} \end{aligned} \quad (1)$$

Modern bond-energy schemes work well with alkanes and substituted alkanes hence we expect good correlation for organometallics which can be regarded as substituted alkanes, e.g. tin alkyls can be considered as alkanes in which a C atom is replaced by Sn and table 1 shows the comparison between observed and calculated  $\Delta_a H^\circ$ 's.

TABLE 1. Observed and calculated  $\Delta_a H^\circ$  values for tin compounds.

	$\Delta_f H^\circ(g)$	$\Delta_a H^\circ(\text{obs})$	$\Delta_a H^\circ(\text{calc})$	$\Delta$
	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$	$\text{kJ mol}^{-1}$
Me <sub>4</sub> Sn	-20.3 ± 1.9	5804.2	5803.1	-1.1
Me <sub>3</sub> SnEt	-29.5 ± 3.0	6966.1	6964.9	-1.2
Me <sub>3</sub> Sn(i-Pr)	-46.8 ± 4.8	8136.0	8135.2	-0.8
Me <sub>3</sub> Sn(t-Bu)	-67.1 ± 6.2	9309.0	9346.1	37.1
Et <sub>4</sub> Sn	-45.3 ± 2.5	10439.9	10450.1	10.2
(n-Pr) <sub>4</sub> Sn	-145.9 ± 5.9	15151.1	15143.1	-8.0
(i-Pr) <sub>4</sub> Sn	-123.1 ± 7.0	15128.3	15131.5	3.3
(n-Bu) <sub>4</sub> Sn	-219.2 ± 4.2	19835.1	19836.2	1.1
Me <sub>3</sub> SnCHCH <sub>2</sub>	91.7 ± 13.4	6408.9	6408.9	0.0
Me <sub>3</sub> SnPh	113.1 ± 5.2	9690.1	9690.1	0.0
Ph <sub>3</sub> SnCHCH <sub>2</sub>	525.5 ± 7.1	18033.1	18069.8	36.7
Ph <sub>4</sub> Sn	572.7 ± 5.6	21288.6	21351.0	62.4

The Laidler scheme was used to calculate  $\Delta_a H^\circ$  with parameters from (ref.1) which list the  $\Delta_f H^\circ(g)$  values. Steric strain is expected in  $\text{Me}_3\text{Sn}(t\text{-Bu})$ ,  $\text{Ph}_3\text{Sn}(\text{CHCH}_2)$  and  $\text{Ph}_4\text{Sn}$ , where  $\Delta_a H^\circ(\text{obs})$  is less than  $\Delta_a H^\circ(\text{calc})$ . This approach is unlikely to apply to coordination complexes because of the change in structure of the ligand on binding to the metal. Moreover, as bond enthalpy values are chosen solely to correlate with  $\Delta_a H^\circ$ , they cannot be regarded as measures of bond strengths.

### BOND DISSOCIATION ENERGIES

The dissociation energy (D) or dissociation enthalpy (DH) of a chemical bond is  $\Delta U$  or  $\Delta H$  for breaking that bond to form radicals,



$$\Delta U = D_1(\text{ML}_{n-1}\text{-L}) : \Delta H = \text{DH}_1(\text{ML}_{n-1}\text{-L}) \quad (3)$$

If all the metal-ligand bonds are broken and they can be regarded as equivalent, then for



$\Delta H/n = \overline{\text{DH}}(\text{M-L})$ , the mean bond dissociation enthalpy. Dissociation enthalpies have relevance in considering reactivity, e.g. in a thermal decomposition the most probable initial step is the rupture of that bond in the molecule with the smallest dissociation enthalpy. The dissociation enthalpy includes the radical reorganization energy (i.e. the energy associated with the difference in structure of the ligand when bound and when free), hence it does not in itself give a fair picture of the strength of chemical binding. Table 2 lists some mean bond dissociation enthalpies in mercury and tin compounds.

TABLE 2. Mean bond dissociation enthalpies  $(\overline{\text{DH}})/\text{kJ mol}^{-1}$

$\text{Me}_2\text{Hg}$	$129.9 \pm 3.0$	$\text{Me}_4\text{Sn}$	$226.4 \pm 1.1$
$\text{Et}_2\text{Hg}$	$102.7 \pm 3.2$	$\text{Et}_4\text{Sn}$	$194.7 \pm 4.4$
$(n\text{-Pr})_2\text{Hg}$	$107.8 \pm 4.0$	$(n\text{-Pr})_4\text{Sn}$	$206.4 \pm 6.0$
$(i\text{-Pr})_2\text{Hg}$	$94.5 \pm 4.5$	$(i\text{-Pr})_4\text{Sn}$	$190.1 \pm 5.5$
$\text{Bz}_2\text{Hg}$	$91.7 \pm 5.0$	$(n\text{-Bu})_4\text{Sn}$	$201.8 \pm 6.0$
$\text{Ph}_2\text{Hg}$	$162.3 \pm 2.5$	$\text{Ph}_4\text{Sn}$	$257.2 \pm 5.4$

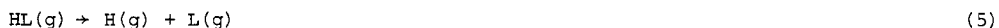
TABLE 3.  $\overline{\text{DH}}(\text{M-L}) - \text{DH}(\text{H-L}) / (\text{kJ mol}^{-1})$  for Hg and Sn compounds

$\text{Me}_2\text{Hg}$	$-308.8 \pm 3.0$	$\text{Me}_4\text{Sn}$	$-212.3 \pm 1.1$
$\text{Et}_2\text{Hg}$	$-307.3 \pm 3.2$	$\text{Et}_4\text{Sn}$	$-215.3 \pm 4.4$
$(n\text{-Pr})_2\text{Hg}$	$-309.9 \pm 4.0$	$(n\text{-Pr})_4\text{Sn}$	$-211.3 \pm 6.0$
$(i\text{-Pr})_2\text{Hg}$	$-311.5 \pm 4.5$	$(i\text{-Pr})_4\text{Sn}$	$-215.9 \pm 5.5$
$\text{Bz}_2\text{Hg}$	$-308.3 \pm 5.0$	$(n\text{-Bu})_4\text{Sn}$	$-212.9 \pm 6.0$
$\text{Ph}_2\text{Hg}$	$-298.2 \pm 2.5$	$\text{Ph}_4\text{Sn}$	$-203.3 \pm 5.4$

The question arises as to whether the variations in  $\overline{\text{DH}}(\text{M-L})$  fairly reflect changes in binding energies or are due to variations in reorganization energies. The effect of reorganization energies can, to a first approximation, be eliminated by considering the dissociation enthalpy of the ligand to the metal relative to the binding to hydrogen, i.e. the difference  $\overline{\text{DH}}(\text{M-L}) - \text{DH}(\text{H-L})$  and this quantity is listed in table 3 for the same mercury and tin compounds.

Table 3 shows that when the metal is bound to a tetrahedral C atom,  $\overline{\text{DH}}(\text{M-L}) - \text{DH}(\text{H-L})$  is constant and in this case we expect the metal-ligand binding energy to be constant. Surprisingly the value changes little for the binding of the metal to a trigonal C atom showing that variation in  $\overline{\text{DH}}(\text{M-L})$  is balanced by that in  $\text{DH}(\text{H-L})$ . Hence we conclude that  $\overline{\text{DH}}(\text{M-L}) - \text{DH}(\text{H-L})$  is effective for considering relative binding energies but there is another and more important motive for examining this quantity: in many cases, especially for the ligands generally involved in coordination complexes,  $\text{DH}(\text{H-L})$  is unknown.

As  $\text{DH}(\text{H-L})$  is  $\Delta_f H$  for



then by combining this with  $\overline{\text{DH}}(\text{M-L})$  from equation (4)

$$\overline{\text{DH}}(\text{M-L}) - \text{DH}(\text{H-L}) = n^{-1} \{ \Delta_f H(\text{M,g}) - \Delta_f H(\text{ML,g}) - \Delta_f H(\text{H,g}) + \Delta_f H(\text{HL,g}) \} \quad (6)$$

The right hand side of equation (6) can be derived relatively easily from experimental measurements, but to derive  $\overline{\text{DH}}(\text{M-L})$ , a value for  $\text{D}(\text{H-L})$  is required. In many instances,  $\text{DH}(\text{H-L})$  is unknown so to proceed a value has to be assumed. The values for copper  $\beta$ -diketonates from ref 2,3 are considered in table 4 together with the iron (III)  $\beta$ -diketonates from ref 4.

TABLE 4.  $\overline{DH(M-L)} - DH(H-L) / (kJ mol^{-1})$  for  $\beta$ -diketonates

Cu(PD) <sub>2</sub>	-83.6 ± 2.4	Fe(PD) <sub>3</sub>	-69.5 ± 3.7
Cu(PIPRM) <sub>2</sub>	-83.8 ± 3.4	Fe(DPM) <sub>3</sub>	-51.7 ± 5.9
Cu(DIBM) <sub>2</sub>	-79.6 ± 3.6	Fe(BZAC) <sub>3</sub>	-68.8 ± 4.6
Cu(IBPM) <sub>2</sub>	-83.8 ± 2.4	Fe(TFAC) <sub>3</sub>	-65.7 ± 7.4
Cu(DPM) <sub>2</sub>	-83.2 ± 6.4	Fe(HFAC) <sub>3</sub>	-57.5 ± 7.9
Cu(BZAC) <sub>2</sub>	-84.6 ± 4.2		
Cu(TROP) <sub>2</sub>	-80.8 ± 10.6		
Cu(TFAC) <sub>2</sub>	-87.0 ± 7.0		
Cu(HFAC) <sub>2</sub>	-91.0 ± 7.8		

PD = pentan-2,4-dionato, PIPRM = 2,2-dimethylheptan-3,5-dionato, DIBM = 2,6-dimethylheptan-3,5-dionato, IBPM = 2,2,6-trimethylheptan-3,5-dionato, DPM = 2,2,6,6-tetramethylheptan-3,5-dionato, BZAC = benzoylacetonato, TROP = tropolonato, TFAC = 1,1,1-trifluoropentan-2,4-dionato, HFAC = 1,1,1,5,5,5-hexafluoropentan-2,4-dionato.

Further examples could be given, for a particular type of ligand the constancy of  $\overline{DH(M-L)} - DH(H-L)$  demonstrates.

(a) Effects influencing  $DH(H-L)$  are compensated in  $\overline{DH(M-L)}$ .

(b) For any metal, measurement of  $\Delta_f H^\circ(g)$  for a single  $\beta$ -diketonate would be sufficient to derive values for other  $\beta$ -diketonates.

(c) For a given ligand type, to make comparisons it is not unreasonable to assume a constant value for  $DH(H-L)$  to derive  $\overline{DH(M-L)}$ . It would be unreasonable to make such comparisons when different types of ligand are involved. Recent work, mainly in Porto and partly in Manchester has been directed towards,

(a) studying complexes of a particular ligand with various metals,

(b) studying complexes of a particular metal with a variety of ligands.

The end result, some distance in the future, will provide reliable estimation of the enthalpy of formation of a coordination compound if not already known. Ribeiro da Silva (ref 5) suggested that the metal-oxygen bonds in  $M(PD)_2$  complexes are similar to the corresponding bonds in metal oxides in which the metal has the same coordination number as in  $M(PD)_2$ . From  $\Delta_r H$  for the decomposition



a parameter,  $\overline{DH(M-O, oxide)} = \Delta_r H/Z$  ( $Z$  = coordination number) can be defined.

Figure 1 shows the correlation between  $\overline{DH(M-L)} - DH(H-L)$  and  $\overline{DH(M-O, oxide)}$  for a series of  $M(PD)_2$  complexes, and this correlation is excellent. Figure 2 shows the corresponding curve for  $M(PD)_3$  complexes and in this case the correlation is reasonably good. Empirical correlations of this type are useful for estimating enthalpies of formation of other metal  $\beta$ -diketonate complexes.

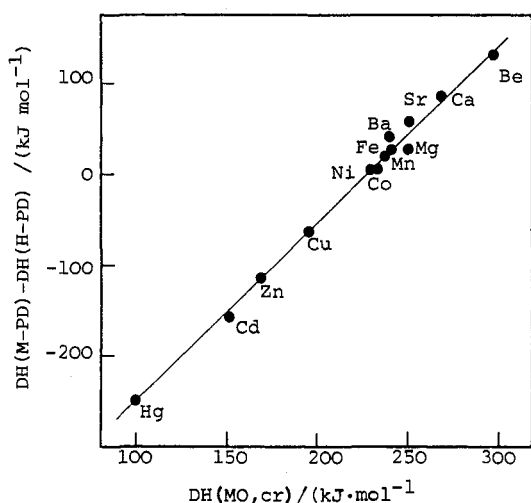


Fig.1. Bis(pentan-2,4-dionates)

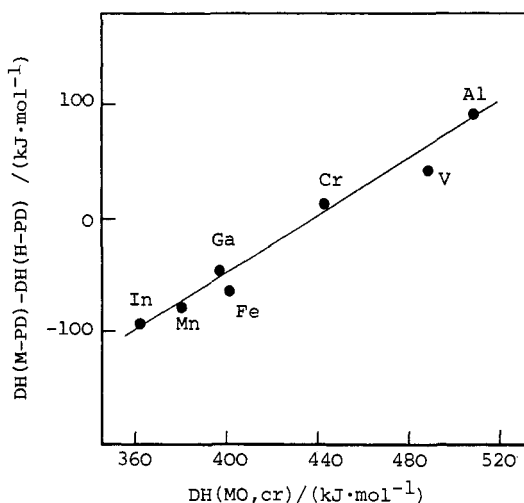
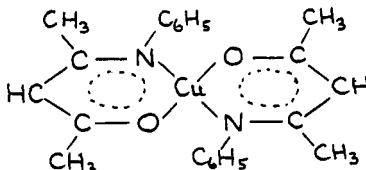


Fig.2. Tris(pentan-2,4-dionates)

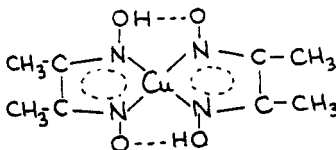
The metal studied so far with the greatest variety of ligands is copper, with the results shown in table 5.

$\text{Cu}(\text{PD})_2$	$-83.6 \pm 2.4$	$\text{Cu}(\text{dimethylglyoximate})_2$	$-63.6 \pm 2.7$
$\text{Cu}(\text{8-OH-quinolate})_2$	$-58.9 \pm 3.0$	$\text{Cu}(\text{PAPD})_2$	$-92.3 \pm 3.8$
$\text{Cu}_2(\text{acetate})_4$	$-66.9 \pm 2.3$	$\text{Cu}(\text{glycinate})_2$	$-26.6 \pm 7.4$

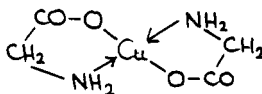
PAPD = 4-phenylamino-3-pentene-2-onato. Taking  $\text{Cu}(\text{PD})_2$  as a base-line, a weakening of the relative binding is expected for  $\text{Cu}(\text{PAPD})_2$  as the structure of this complex



shows possibilities of steric hindrance. The remaining complexes show a strengthening of relative binding compared with  $\text{Cu}(\text{PD})_2$ . In  $\text{Cu}_2(\text{acetate})_4$  the possibility of a (Cu-Cu) bond is controversial and the thermochemical results suggest that if this does exist, it will not be strong. In the dimethylglyoxime complex the two intramolecular hydrogen bonds leads to strengthening of the relative binding energy.



The most surprising result is for copper glycinate which compared with  $\text{Cu}(\text{PD})_2$  shows an increased relative binding strength of  $57 \text{ kJ mol}^{-1}$ .



There is no obvious explanation, an apparently similar situation is observed for nickel,  $\overline{DH}(\text{Ni-L}) - \overline{DH}(\text{H-L}) / (\text{kJ mol}^{-1})$ ,  $\text{Ni}(\text{PD})_2 = -14 \pm 3$ ,  $\text{Ni}(\text{glycinate})_2 = 26 \pm 5$ .

### CORRELATIONS FOR ENTHALPIES OF FORMATION

For complexes  $\text{ML}_n$ , for a particular type of ligand and a given metal, if  $\overline{DH}(\text{M-L}) - \overline{DH}(\text{H-L})$  is constant, it then follows from equation (6) that  $\Delta_f H^\circ(\text{ML}_n, \text{g}) - n\Delta_f H^\circ(\text{HL}, \text{g})$  will be constant. Hence a plot of  $\Delta_f H^\circ(\text{ML}_n, \text{g})$  against  $\Delta_f H^\circ(\text{HL}, \text{g})$  should be linear of slope  $n$ . This plot for the  $\beta$ -diketonates of copper (figure 3) has slope  $(1.99 \pm 0.01)$  and for the  $\beta$ -diketonates of Fe(III), slope  $(3.01 \pm 0.01)$ , of Cr(III), slope  $(3.10 \pm 0.01)$  are shown in figure 4.

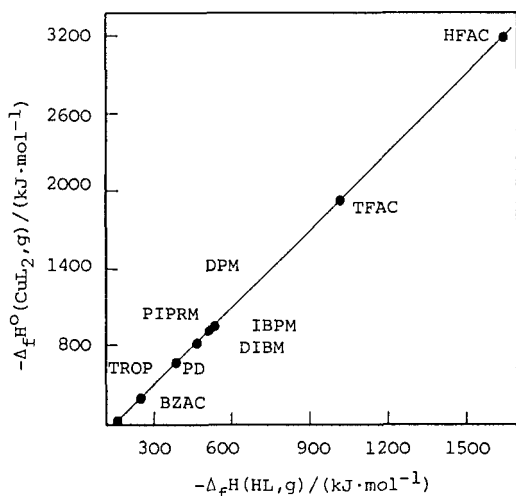


Fig.3.  $\text{Cu}(\beta\text{-diketonates})$ : symbols as in text

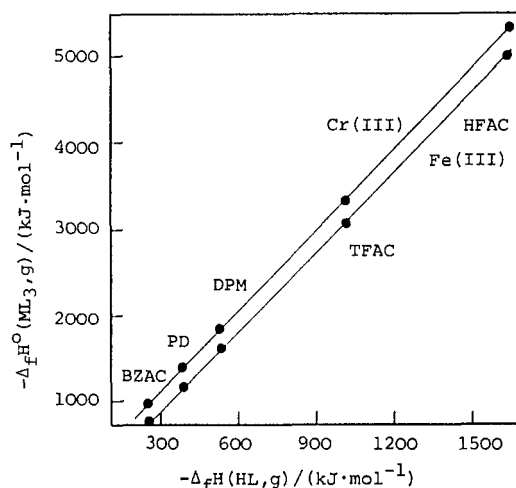


Fig.4. Cr and Fe tris( $\beta$ -diketonates)

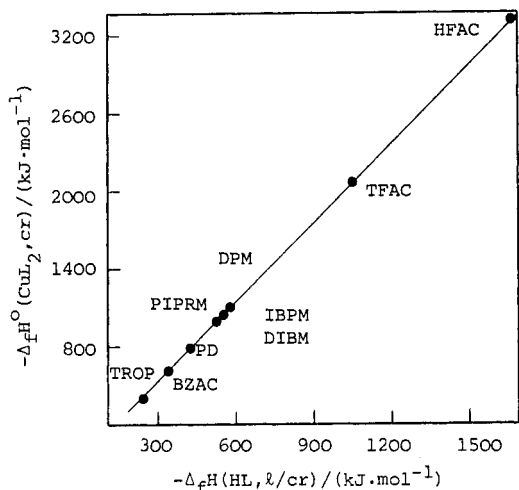


Fig.5. Cu(β-diketonates): condensed state

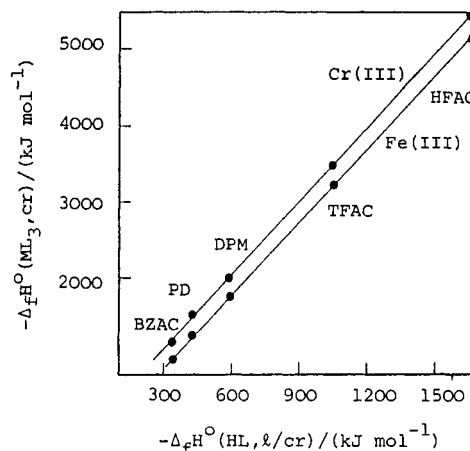


Fig.6. Cr, Fe(β-diketonates), condensed state.

We can also consider the situation in the condensed state as

$$\Delta_f H^\circ(\text{ML}_n, \text{g}) - n\Delta_f H^\circ(\text{HL}, \text{g}) = \Delta_f H^\circ(\text{ML}_n, \text{cr}) - n\Delta_f H^\circ(\text{HL}, \text{cr}/\ell) + \Delta H_{\text{sub}}(\text{ML}_n) - n\Delta H_{\text{sub}}(\text{HL}) \quad (8)$$

It is reasonable to expect the difference between the sublimation terms to be approximately constant, hence  $\Delta_f H^\circ(\text{ML}_n, \text{cr})$  plotted against  $\Delta_f H^\circ(\text{HL}, \text{cr}/\ell)$  should be linear of slope  $n$ . This plot for the β-diketonates of copper has slope  $(2.02 \pm 0.02)$ , figure 5; and for the β-diketonates of Fe(III), slope  $(3.06 \pm 0.02)$  and for Cr(III), slope  $(3.17 \pm 0.02)$  are shown in figure 6.

Such plots have value in critically examining thermochemical data, those for amino acid complexes are shown in figure 7. For the copper complexes, the line of slope 2 is drawn through the values determined in Porto (ref.6). The remaining values, Bernard et al. (ref.7) do not fit this line and the slope through the Ni values is certainly not 2. A systematic study of amino acid complexes would be a worthwhile project.

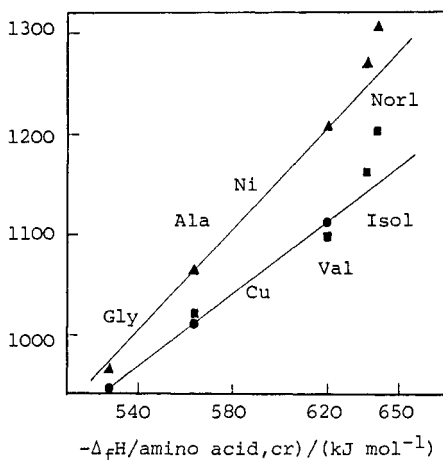


Fig.7. Amino acid complexes condensed state.

M.A.V. Ribeiro da Silva ref.6.

Bernard et al. ref.7.

Gly = glycine, Ala = α-alanine,

Val = valene, Isol = isoleucine,

Norl = norleucine

Thermochemists are most content when dealing with the gaseous state and estimation of values for condensed states are generally difficult usually involving guessing an enthalpy of sublimation. Further tests are needed but if the relations as demonstrated in figures 5,6 are generally applicable, a very simple method of estimating  $\Delta_f H^\circ$  of a coordination complex in the solid state is available. The requirement is  $\Delta_f H^\circ(\text{ML}_n, \text{cr})$  for one complex of the metal containing the appropriate type of ligand, then from the curve of  $\Delta_f H^\circ(\text{ML}_n, \text{cr})$  versus  $\Delta_f H^\circ(\text{HL}, \ell/\text{cr})$  of slope  $n$ , values for complexes of other ligands can be estimated from  $\Delta_f H^\circ(\text{HL}, \ell/\text{cr})$ . If the latter is unknown it would be easy to estimate as it will be an organic molecule.

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