Thermodynamic Study on Oxime Complexes: The Relative Co-ordinating Power of Ketone, Oxime, and Amine Functional Groups

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Thermodynamic data (ΔG, ΔH, ΔS) are reported for the reaction of the diamine-dioxime 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dioxime with protons and copper(II) ions in aqueous solution. Data for the formation of the copper complexes are compared with data for the analogous diamine-diketone 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione and the analogous tetra-amine 2,11-diamino-4,4,9,9-tetramethyl-5,8-diazadodecane. The relative co-ordinating powers of different donor groups in these structurally related ligands are amine > oximato ~ oxime > ketone (~H_2O).

THE role of the oxime functional group in quantitative inorganic analysis is well known.[1] The most important application is the use of *vic*-dioximes [*e.g.* dimethylglyoxime, α-furil dioxime, cyclohexane-1,2-dione dioxime-(nioxime), salicylaldoxime] as organic precipitants for the gravimetric determination of Ni and Pd in aqueous solution.[1,2] As a consequence of this analytical application, *X*-ray diffraction,[3,4] spectroscopic,[5,6] and magnetic studies [7,8] have been reported for several transition-metal bis(*vic*-dioxime) complexes. These studies indicated a general square planar structure and the existence of stable oxime-oximato $C{=}N{-}OH \cdots \bar{O}{-}N{=}C$, hydrogen bridges. The low solubility of those complexes utilised in gravimetric analysis is related to the existence of metal–metal interactions between metal ions in square planar co-ordination.[9] Despite the weak basicity of oxime groups, the bisdimethylglyoxime complexes of Fe^{II} and Ni^{II} are diamagnetic, indicating that the ligand generates a strong ligand field.[8]

From equilibrium studies on transition-metal dimethylglyoxime complexes,[8,10-12] the ratio of the two stepwise stability constants ($\log K_1/\log K_2 \leqslant 1$) suggests that the oxime-oximato hydrogen bridges make a significant contribution to the bis-complex stability [for most bidentate ligands $K_1 \gg K_2$,[13] *e.g.* for $Cu(en)_2^{2+}$ $\log K_1 = 10{\cdot}48$, $\log K_2 = 9{\cdot}08$, 25 °C $I = 0$ [14]]. The stability of the 1 : 1 iron(II) dimethylglyoxime complex exceeds that predicted from the Irving–Williams stability order.[8] This has been attributed to the existence of π-back-bonding from the metal ion to the oxime group, an effect which will be strongest for iron(II).[8] Evidence from infrared,[15] ultraviolet–visible,[15] and e.p.r.[16] spectroscopic studies also suggests the formation of π-bonding in transition-metal–(dimethylglyoxime) complexes.

Although *vic*-dioxime complexes have been extensively studied, there are insufficient thermodynamic data to allow a comparison of the donor power of a non-conjugated oxime group with that of other functional groups. Earlier publications [17-19] reported the preparation of three related quadridentate ligands, a diamine-diketone (1), a diamine-dioxime (2), and a tetra-amine (3). The acid salts of these compounds are water soluble and the basic secondary amine groups in (1) and (2) allow the ligand co-ordination reactions to be readily followed by pH potentiometry. A comparison of the thermodynamic data for complex formation of these ligands indicates

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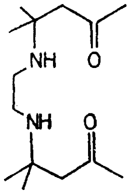
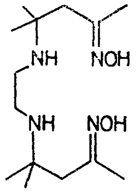
the relative co-ordinating power of the ketone, oxime, and amine functional groups.



(1)



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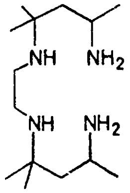

(3)

The amine group protonation constants for the diamine-dioxime ligand, LH_2(2), and the equilibrium constants for the reactions $Cu^{2+} + LH_2 \rightleftharpoons Cu(LH_2)^{2+}$ and $Cu(LH_2)^{2+} \rightleftharpoons Cu(LH)^+ + H^+$, have been reported.[20] In this paper we report enthalpy data for these reactions, and protonation constants and the copper complex stability constant for the diamine-diketone ligand (1). Data for the formation of these copper complexes are compared with previously reported thermodynamic data for the formation of the copper(II) complex with the tetra-amine hm-3,2,3-tet(3).[21] For the protonation of LH_2, data are interpreted in terms of the structure of the ligand.

EXPERIMENTAL

Materials.—The preparations of the diamine-dioxime and diamine-diketone ligands have been described.[17,18] Standard solutions of copper chloride were obtained as previously described.[22]

p[H$^+$] *Measurements.*—p[H$^+$] data were obtained by potentiometric titrations using the apparatus and [H$^+$] calibration method described previously.[23]

Calorimetric Measurements.—The calorimeter and its operation have been described.[22] For the protonation of the diamine-dioxime ligand, solutions of the ligand at pH ~ 10 ($T_L \sim 5 \times 10^{-3}$M) were titrated with standard HCl (~0·5M) and for the copper–(diamine-dioxime) complexes solutions of the complex $Cu(LH)^+$ ($T_M \sim 3 \times 10^{-3}$M) were titrated with standard HCl (~1M).

RESULTS AND CALCULATIONS

Stability Constants.—Representative p[H$^+$] data from the titrations of NaOH against solutions of the diamine-dioxime ligand and HCl, and against solutions of the diamine-diketone ligand and HCl, are deposited with the National Lending Library.[24]

In aqueous solutions, in the pH range 4—7 the diamine-diketone ligand decomposed slowly (*ca.* 0·5% h^{-1}) producing mesityl oxide. (At pH *ca.* 4·5 the measured pH was stable to ±0·006 pH over a period of 8 h.) However, in the pH range 7·5—10 there was a marked increase in the rate of decomposition; in this alkaline region only two or three reliable data points could be obtained from any titration.

Protonation constants were calculated from the $\bar{n}_H$, p[H$^+$] against solutions of the diamine-diketone, copper ions, and HCl are deposited with the National Lending Library.[24] For each titration the experimental end point suggested the formation of a 1 : 1 metal : ligand complex $Cu(L)^{2+}$. The stability constant for the formation of $Cu(L)^{2+}$ was calculated from the data at each titration point. The mean log K and standard deviation for titrations at $T_L \sim 6{\cdot}1 \times 10^{-4}$M, $T_M \sim 3{\cdot}8 \times 10^{-4}$M and $T_L \sim 7{\cdot}9 \times 10^{-4}$M, $T_M \sim 7{\cdot}6 \times 10^{-4}$M were $8{\cdot}55_6 \pm 0{\cdot}02$ and $8{\cdot}56_3 \pm 0{\cdot}02$ respectively. Representative p[H$^+$] data from the titrations of NaOH against solutions of the diamine-dioxime, copper(II) ions, and HCl are also deposited as supplementary material.[24]

TABLE 1

Protonation constants for the diamine-dioxime and diamine-diketone ligands at 25 °C, NaCl solution

	Diamine-dioxime	
Ionic strength (M)	log k_4 [a]	log k_3 [a]
0·20	6·46 ± 0·02 [b]	9·47 ± 0·02
0·15	6·40 ± 0·02	9·43 ± 0·02
0·10 [c]	6·35 ± 0·02	9·41 ± 0·02
0·04	6·20 ± 0·02	9·37 ± 0·02
0·00	5·89 [d] ± 0·02	9·35 [e] ± 0·02
	Diamine-diketone	
Ionic strength	log k_2 [f]	log k_1 [f]
0·10	6·19 ± 0·02	9·41 ± 0·04

[a] $k_3 = [LH_3^+]/[LH_2][H^+]$, $k_4 = [LH_4^{2+}]/[LH_3^+][H^+]$. [b] Uncertainties were estimated from the standard deviation of log k_1 for a number of titrations and from solution composition uncertainties. [c] Data from ref. 20. [d] From a plot of log $k_4 - 2\sqrt{I}/(1 + \sqrt{I})$ against I. [e] From a plot of log k_3 against I. [f] $k_2 = [LH_2^{2+}]/[LH^+][H^+]$, $k_1 = [LH^+]/[L][H^+]$.

Enthalpy Data.—All calorimetric titration data are deposited with the National Lending Library.[24] The procedures used to calculate the solution composition at each titration point, and the stepwise enthalpies of protonation, have been described.[22] The stepwise enthalpy changes are shown in Table 2.

For the calorimetric titrations of HCl against solutions of the diamine-dioxime complex $Cu(LH)^+$ the heat change per mole of HCl added (the difference between exothermic and endothermic terms) was small, and only one or two titration points could be measured for each run. The solution composition at each titration point was calculated by a successive approximations method incorporated into a suitable computer program. The enthalpy changes for the formation of $Cu(LH_2)^{2+}$ and $Cu(LH)^+$ were then calculated by a least-squares process as outlined previously.[22] The thermodynamic functions for the formation of these complexes are shown in Table 3.

Because of the decomposition of the diamine-diketone ligand, no calorimetric study of this compound was attempted.

DISCUSSION

Diamine-dioxime Protonation.—The diamine-dioxime ligand protonation constants and give copper(II) complexes with identical formation constants.[20] Additional spectroscopic data and evidence from synthetic work suggest that isomerisation is rapid in aqueous solution containing acids, bases, or metal ions.[18] The oxime nitrogen atom is very weakly basic [20] [pK (=N$^+$HOH) $\leqslant$ 2] and the basicity of this group is not considered in the following discussion.

The free-energy data in Table 2 show that there is a considerable reduction in the basicity of the secondary amine nitrogen compared with that for *NN'*-dimethylethylenediamine.[25] The enthalpy data for the diamine-dioxime ligand show a corresponding decrease in the exothermic heats of protonation, when compared with data for *NN'*-dimethylethylenediamine protonation.[26] This decrease arises from the effect of the increased length of the alkyl chains in the diamine-dioxime and also from the effect of the two oxime substituents. Empirical formulae have been proposed [27-29] for calculation of the enthalpy changes for protonation of amines. Using the formula recently reported by Paoletti and his co-workers,[29] the predicted stepwise enthalpies of protonation of the diamine, $[Me(CH_2)_2{\cdot}C(Me)_2{\cdot}NH{\cdot}CH_2{\cdot}]_2$, which has a structure identical to that of the diamine-dioxime ligand, without the oxime substituents, are $-51{\cdot}5_6$ and $-47{\cdot}4_8$ kJ mol^{-1} for ΔH_1 and ΔH_2 respectively. The differences between these values and the enthalpies of protonation of the diamine-dioxime ligand (Table 2), can be related, in part, to the base-weakening effect of the electron-withdrawing oxime substituents.

TABLE 2

Thermodynamic data for stepwise protonation of the diamine-dioxime ligand at 25 °C, I = 0·00M

Reaction	log k^0	$-\Delta G°$/kJ mol^{-1}	$-\Delta H°$/kJ mol^{-1} [a]	$\Delta S°$/J mol^{-1} K^{-1}
$LH_2 + H^+ \rightleftharpoons LH_3^+$	9·35 ± 0·02	53·4 ± 0·1	39·6 ± 0·3	46 ± 1
$LH_3^+ + H^+ \rightleftharpoons LH_4^{2+}$	5·89 ± 0·02	33·6 ± 0·1	39·4 ± 0·3	−19 ± 1

Thermodynamic data [b] for stepwise protonation of *NN'*-dimethylethylenediamine at 25 °C, I = 0·00M

Reaction	log k^0	$-\Delta G°$/kJ mol^{-1}	$-\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}
$L + H^+ \rightleftharpoons LH^+$	10·03	57·2	44·9	41·3
$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	6·79	38·8	39·0	−0·8

[a] Enthalpy data were determined at I = 0·10M and corrected to infinite dilution [H. K. J. Powell and N. F. Curtis, *J. Chem. Soc.* (*B*), 1966, 1205]. [b] log k Data from ref. 25. ΔH Data from ref. 26 were corrected to infinite dilution (*loc. cit.*).

TABLE 3

Thermodynamic data for the formation of copper(II) complexes with the diamine-dioxime and diamine-diketone ligands at 25 °C and I = 0·10M

Reaction	log K_1	$-\Delta G$/kJ mol^{-1}	$-\Delta H$/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
Diamine-dioxime				
$Cu^{2+} + LH_2 \rightleftharpoons Cu(LH_2)^{2+}$	13·24[a] ± 0·05	75·6 ± 0·3	54·8 ± 0·3	70 ± 2
$Cu(LH_2)^{2+} \rightleftharpoons Cu(LH)^+ + H^+$	−3·23 ± 0·08	−18·4 ± 0·5	−23·7 ± 0·3	18 ± 3
Diamine-diketone				
$Cu^{2+} + L \rightleftharpoons Cu(L)^{2+}$	8·56 ± 0·05	$48{\cdot}8_5 \pm 0{\cdot}3$		

[a] Diamine-dioxime log K data from ref. 20.

For the diamine-dioxime ligand $\Delta H_1° = \Delta H_2°$, within experimental error, whereas for most diamines [27,28] $\Delta H_1° > \Delta H_2°$. Oxime groups are good hydrogen-bond donors while amines are good hydrogen-bond acceptors.[30] The approximate equality of the stepwise enthalpy changes may be due to the formation of an intramolecular hydrogen bonding interaction in the free ligand between the unprotonated amine and the oxime function. This interaction would cause a slight reduction in the amine basicity for the first stepwise protonation which may account for the approximate equality of $\Delta H_1°$ and $\Delta H_2°$.

The second stepwise entropy change $\Delta S_2°$ for protonation of the diamine-dioxime is more negative than that for *NN'*-dimethylethylenediamine; this could result, in part, from the greater loss in configurational entropy of the alkyl chains due to chain stiffening.[31] In contrast $\Delta S_1°$ is similar for the two diamines as might result from opposing effects of chain-stiffening and loss of hydrogen bonding for the diamine-dioxime.

Copper(II) *Diamine-dioxime Complexes*.—Structural studies have shown that the diamine-dioxime ligand coordinates in the *syn*-form in the solid state.[20] Evidence from electronic spectra suggests that the mode of coordination is also *syn* in aqueous solution.[20]

The stability constant for the formation of the copper-(diamine-dioxime)complex $Cu(LH_2)^{2+}$ (Table 3) is greater than that for Cu(*NN'*-dimethylethylenediamine)$^{2+}$ (log $K_1 = 10{\cdot}10_7$,[32] 0·5M-KNO$_3$, 25 °C), despite the lower basicity of the diamine-dioxime ligand, but is less than that for the related tetra-amine complex Cu(hm-3,2,3-tet)$^{2+}$ (log K_1 = 22·41,[21] 0·1M-NaCl, 25 °C). This indicates that the two oxime functions make a significant

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contribution to the stability of $\mathrm{Cu(LH_2)^{2+}}$ yet the oxime function, C=NOH, is a much weaker donor that $-\mathrm{NH_2}$.

If the oxime functions were not co-ordinated, then the ratio of the enthalpy change on formation of $\mathrm{Cu(LH_2)^{2+}}$ to the overall enthalpy of protonation of the diamine-dioxime ligand would be similar to the corresponding ratio for *NN'*-dimethylethylenediamine. Using the enthalpies of protonation for the two ligands (*NN'*-dimethylethylenediamine data at 0·5M-$\mathrm{KNO_3}$, 25 °C [26]) and the enthalpy of formation of Cu(*NN'*-dimethylethylenediamine)$^{2+}$ [32] the predicted enthalpy of formation of $\mathrm{Cu(LH_2)^{2+}}$ is $-43·4$ kJ mol^{-1}. A comparison of this value with the experimentally determined value suggests that the co-ordination of the two oxime functions contributes $-11·4$ kJ mol^{-1} to the enthalpy of formation of $\mathrm{Cu(LH_2)^{2+}}$.

The entropy change for the formation of $\mathrm{Cu(LH_2)^{2+}}$ is of a similar magnitude to those for the formation of Cu(hm-3,2,3-tet)$^{2+}$ (80·2 J mol^{-1} K^{-1}) and Cu(3,2,3-tet)$^{2+}$ (66·3 J mol^{-1} K^{-1}); this is consistent with the proposed co-ordination of all four donors in $\mathrm{Cu(LH_2)^{2+}}$. [The entropy of formation of Cu(*NN'*-dimethylethylenediamine)$^{2+}$ is 37·7 J mol^{-1} K^{-1}.[32]]

The hydroxy-group of an oxime function is very weakly acidic; the pK_a for proton dissociation from $\mathrm{LH_2}$ has been estimated as 12·3.[20] The log K data in Table 3 show that on co-ordination to the copper ion there is a marked increase in the acidity of the oxime proton. The enthalpy change for the proton dissociation $\mathrm{LH_2 \rightleftharpoons LH^- + H^+}$ has not been determined. However, by analogy with similar studies on some pyridine-2-carbaldehyde oxime–iron(II) complexes,[33] the marked increase in the oxime acidity in $\mathrm{Cu(LH_2)^{2+}}$ is probably due to a more favourable enthalpy contribution to the dissociation reaction; this could arise from stabilisation of the resonance forms of $-\mathrm{C{=}N{-}\bar{O}}$ (by charge redistribution) by the metal ion. The occurrence of a solvent-dependent charge-transfer transition for $\mathrm{Cu(LH)^+}$ suggests that charge redistribution is important.[20] The formation of an intraligand oxime-oximato hydrogen bond in $\mathrm{Cu(LH)^+}$ will also contribute to the increase in the acidity of the oxime proton.

Stability constant data were obtained from solutions with $T_\mathrm{M} : T_\mathrm{L}$ ratios of 1 : 1·5, 1 : 2, and 1 : 3 and also at different total metal ion concentrations.[20,24] The least-squares analysis of each set of titration data gave reproducible equilibrium constants for $\mathrm{Cu^{2+} + LH_2 \rightleftharpoons Cu(LH_2)^{2+}}$ and for $\mathrm{Cu(LH_2)^{2+} \rightleftharpoons Cu(LH)^+ + H^+}$, which indicated the absence of polynuclear complex formation under these experimental conditions. The mean and standard deviation from the mean of the constants obtained for each titration have been reported previously.[20]

The Copper(II) *Diamine-diketone Complex*.—Although the basicity of the diamine-diketone ligand is similar to that of the diamine-dioxime (Table 1) the stability constant for the 1 : 1 copper–(diamine-diketone) complex $\mathrm{Cu(L)^{2+}}$ is only $8·56 \pm 0·05$. The energy of the *d–d* transition for the complex ($\lambda = 648$ nm) is similar to that for other copper(II) complexes with two nitrogen and two oxygen donors in planar co-ordination in aqueous solution,[34] however additional evidence is required to confirm that the ketone functions, and not water molecules, are co-ordinated in the third and fourth co-ordination sites.

Martell and his co-workers [35] have shown that the pK' values for proton dissociation from co-ordinated water molecules in 1 : 1 copper chelates of a number of carbon and nitrogen substituted ethylenediamines lie in the narrow range 7·1—7·5, suggesting that proton dissociation is relatively independent of the stability of the 1 : 1 chelate. Analysis of the pH titration curves from the copper–(diamine-diketone) system indicated that no $\mathrm{CuL(OH)^+}$ was formed, which indirectly supports the proposed co-ordination of the ketone functions. A comparison of the ratio of the copper(*NN'*-di-n-propylethylenediamine)$^{2+}$ complex stability to the ligand basicity [log K/Σ log $k_\mathrm{i} = 8·79/17·80$, 0·5M-$\mathrm{KNO_3/Ba(NO_3)_2}$, 25 °C] [36] with the corresponding ratio for the diamine-diketone (8·56/15·60) indicates that the copper–(diamine-diketone) complex is more stable than expected on the basis of ligand basicity alone, again suggesting that the ketone functions are co-ordinated.

Comparison of the Oxime, Amine, and Ketone Functional Groups.—Although no enthalpy data are available for the protonation and complex formation of the diamine-diketone ligand, trends in the log K data will reflect the donor power of the functional groups.

The low value of log K for the copper-(diamine-diketone) complex indicates that the ketone function is a weak donor to copper(II) ions and perhaps is only a slightly better donor that a water molecule. The oxime groups make a measurable contribution to the stability of the $\mathrm{Cu(LH_2)^{2+}}$ complex. It is interesting to note that, by combining the pK value (12·3) for proton dissociation from the diamine-dioxime,[20] $\mathrm{LH_2 \rightleftharpoons LH^- + H^+}$, with the log K data for the formation of the copper complexes (Table 3), the stability constant for the reaction $\mathrm{Cu^{2+} + LH^- \rightleftharpoons Cu(LH)^+}$ is estimated as log $K = 22·3$. However, the difference of 10^9 between this stability constant and that for $\mathrm{Cu^{2+} + LH_2 \rightleftharpoons Cu(LH_2)^{2+}}$ (Table 3) is not attributable to the increased donor power of an oximato-group, for results from visible absorption spectra suggest that the ligand-field strengths are similar in both the $\mathrm{Cu(LH_2)^{2+}}$ and $\mathrm{Cu(LH)^+}$ complexes ($\lambda_\mathrm{max.} = 592$ and 583 nm respectively).[20] The bulk of this 10^9 (51·4 kJ mol^{-1}) is probably the result of intramolecular hydrogen bond formation. (The binding energy relative to $\mathrm{H_2O}$ and $\mathrm{OH^-}$, for $\mathrm{[HOHOH]^-}$ at an O–O separation of 2·51 Å has been calculated to be

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101·7 kJ mol^{-1}.[37]) The high value of log *K* for the Cu(lm-3,2,3-tet)$^{2+}$ complex (22·4) manifests the strong donor power of an amine functional group. Although differences among the stability constants for all these complexes will also incorporate terms arising from structural differences in the chelate rings, these terms will be comparatively small and the order of donor strength of the functional groups, as indicated by the log *K* data, is $H_2O \sim$ ketone $\ll$ oxime $\sim$ oximato $\ll$ amine.

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