# Thermal, Spectroscopic, and Structural Properties† of Aqua(malonato-*O,O'*)(1,10-phenanthroline)copper(II) Hydrate (1/1.5)

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Aqua(malonato-*O,O'*)(1,10-phenanthroline)copper(II) crystallizes in the triclinic space group $P\bar{1}$ with $a$ = 11.560(4), $b$ = 11.734(5), $c$ = 12.491(2) Å, $\alpha$ = 92.12(2), $\beta$ = 105.50(2), $\gamma$ = 109.28(3)°, and $Z$ = 2. The structure consists of two independent monomeric [Cu(phen)(mal)($H_2O$)] molecules with three water molecules in the lattice. The $CuN_2O_2O'$ chromophore is distorted square pyramidal with a symmetrically co-ordinated phen molecule (mean Cu–N 2.018 Å) and a symmetrically co-ordinated malonate ion (mean Cu–O 1.914 Å) in the plane of the square pyramid and a water molecule at 2.266 Å. The relatively short Cu–O distance has been attributed to phen being a stronger $\pi$-acid. The compound and its several related complexes show complete loss of water molecules at *ca.* 100 °C followed by stepwise degradation of the organic ligands. Thermogravimetric analysis and visible reflectance spectral results are discussed in relation to the known structure of the title compound.

Ternary complexes of the copper(II) ion containing an $\alpha,\alpha'$-diimine and an oxygen-donor ligand have been extensively investigated.[1—5] Recently it has been reported[6] that the complex containing the 2,2'-bipyridyl (bipy) and the oxalate ion (ox) exists in two forms [Cu(bipy)(ox)($H_2O$)]·$2H_2O$ (**A**) and [Cu(bipy)(ox)]·$2H_2O$ (**B**). *X*-Ray structural analyses demonstrate that the former consists of a monomeric copper(II) ternary complex while the latter contains a bridging oxalate ion. In view of the close structural similarities between 1,10-phenanthroline (phen) and bipy as well as between malonate and oxalate, the ternary complex [Cu(phen)(mal)($H_2O$)] has now been re-examined through thermogravimetric analysis (t.g.a.), spectroscopic and structural measurements. As there have been few studies on the thermoanalytical behaviour of these complexes the t.g.a. has been carried out on several related complexes in the present investigation. Such results are useful in understanding the properties and structural characteristics of the complexes in the solid state.

## Experimental

*Preparation of Complexes.*—The complexes were prepared according to the methods described earlier.[7,8] Crystals of [Cu(phen)(mal)($H_2O$)]·$1.5H_2O$ were obtained by slow evaporation of a water–methanol (3:2) solution. A blue crystal of approximate dimensions 0.12 × 0.42 × 0.47 mm was sealed in a 0.5-mm glass capillary tube for *X*-ray data collection.

*Physical Measurements.*—The reflectance spectra of the solid complexes were recorded using a Shimadzu UV 240 spectrophotometer and a Perkin-Elmer Lambda 9 u.v.–visible–near i.r. spectrophotometer equipped with a standard reflectance attachment. The i.r. spectra (4 000—200 $cm^{-1}$) obtained from KBr or CsI pellets were recorded with a Perkin-Elmer 599 spectrophotometer. T.g.a. measurements were performed on a Perkin-Elmer TGS-1 thermobalance with a temperature programmer (UU-1) capable of operating up to 1 000 °C. The dynamic runs were carried out at a heating rate of 10 °C $min^{-1}$, unless otherwise stated, in static air, on samples of between 3 and 7 mg in weight. For the determination of activation energy, the isothermal runs were conducted at 170, 175, 180, 185, and 190 °C.

*X-Ray Data Collection and Structure Determination.*—Preliminary cell dimensions were determined using 25 accurately centred reflections obtained from the Enraf-Nonius program package SEARCH. Refined cell dimensions and their estimated standard deviations were estimated from least-squares refinement of accurately centred reflections in the range $20 < 2\theta < 22°$. The diffraction data in the range $0 < 2\theta < 44°$ were collected at room temperature on an Enraf-Nonius CAD4A diffractometer using Mo-$K_\alpha$ radiation. A summary of crystal data and intensity collection is given in Table 1.

The structure was solved by Patterson and difference-Fourier methods using the computer programs of the Enraf-Nonius structure determination package. Least-squares refinement of positional and anisotropic thermal parameters for all the non-hydrogen atoms led to convergence at $R$ = 0.047 and $R'$ = 0.064. The positions of the hydrogen atoms on the malonate and phenanthroline were calculated from standard geometries. The hydrogen atoms whose positions were calculated were given isotropic thermal parameters of 5.0 $Å^2$ and were used in the structure factor calculations without further refinement. The hydrogen atoms of the water molecules were not located in the difference map nor were their positions calculated. The final positional parameters are given in Table 2.

## Results and Discussion

*Description of the Structure.*—The asymmetric unit consists of two molecules of the complex [Cu(phen)(mal)($H_2O$)] and three water molecules of crystallisation. Figure 1 shows the perspective view of [Cu(phen)(mal)($H_2O$)]·$1.5H_2O$ together with the atom numbering scheme and atomic vibrational

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† *Supplementary data available* (No. SUP 56604, 5 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

**Table 1.** Summary of crystal data and intensity collection for [Cu(phen)(mal)($H_2O$)]·1.5$H_2O$

| | |
|---|---|
| Formula | $C_{15}H_{15}CuN_2O_{6.5}$ |
| *M* | 390.8 |
| *a*/Å | 11.560(4) |
| *b*/Å | 11.734(5) |
| *c*/Å | 12.491(2) |
| α/° | 92.12(2) |
| β/° | 105.50(2) |
| γ/° | 109.28(3) |
| *U*/Å$^3$ | 1 526.5 |
| *Z* | 2 |
| $D_c$/g cm$^{-3}$ | 1.505 |
| Space group | $P\bar{1}$ |
| Crystal dimensions (mm) | *ca.* 0.12 × 0.42 × 0.47 |
| Temperature (°C) | 23 |
| Radiation | Mo-$K_\alpha$, with graphite monochromator |
| λ/Å | 0.710 73 |
| μ(Mo-$K_\alpha$)/cm$^{-1}$ | 15.057 |
| *F*(000) | 800 |
| Scan mode | θ–2θ |
| 2θ range (°) | 0 < 2θ < 44 |
| Reflections collected | 3 964 |
| Unique reflections ($F^2 > 3\sigma F^2$) | 2 759 |
| Final no. of variables | 442 |
| *R* | 0.047 |
| *R'* | 0.064 |
| E.s.d. in an observation of unit weight | 2.009 |

ellipsoids. Selected bond distances and bond angles involving the copper(II) ion are listed in Table 3. All water molecules are hydrogen bonded with one another or with the oxygen atoms of the carboxylate group.

The geometry around the copper(II) ion is five-co-ordinate distorted square pyramidal. Both the phenanthroline molecule and malonate ion are symmetrically co-ordinated (mean Cu–N 2.018, mean Cu–O 1.914 Å), with the four atoms in the equatorial plane, the N atoms of the phenanthroline and one oxygen atom from each of the carboxylate of malonate showing very small deviations of 0.024, −0.023, −0.016, and 0.014 Å respectively. The copper(II) ion is raised above the equatorial plane N(1),N(2),O(1),O(2) by 0.192 Å towards the apical oxygen from this basal plane. The Cu to apical oxygen bond is not significantly tilted away from the normal to the basal plane [O(1V)–Cu–N(1) 95.98(13), O(1V)–Cu–N(2) 93.86(14), O(1V)–Cu–O(1A) 98.73(14), and O(1V)–Cu–O(2A) 93.92(13)°]. The water molecule occupying the fifth co-ordination position is at 2.266 Å. This is somewhat shorter than that reported for [Cu(bipy)(ox)($H_2O$)]·2$H_2O$[6] and those for other similar copper(II) complexes.[9–11] The dihedral angle between the two planes N(1)–Cu–N(2) and O(1)–Cu–O(2) is 15.9°. The N ··· N 'bite' of phen is 2.62 Å which falls in the normal range.[12–15] Moreover the bite angle N–Cu–N of 81° is close to those (80.6, 81°) reported for bipy in square-pyramidal Cu$^{II}$ complexes.[6] On comparison with other reported structures of complexes containing phen,[16–18] there are no unusual bond angles or bond lengths. Comparing this structure with that[6] of [Cu(bipy)(ox)($H_2O$)]·2$H_2O$, it is seen that the Cu–N(phen) distance is longer and Cu–O(carboxylate) is shorter in [Cu(phen)(mal)($H_2O$)]·1.5$H_2O$ (Table 3). Furthermore the Cu–O distances [1.909(3) and 1.919(3) Å] are relatively short among the malonate complexes (Table 4). This is probably a manifestation of the stronger π-acceptor character of phen which in turn results in a greater sharing of electron density of mal with the copper(II) centre.

**Table 2.** Positional parameters for [Cu(phen)(mal)($H_2O$)]·1.5$H_2O$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu(1) | 0.295 12(7) | 0.432 26(6) | 0.025 71(6) |
| Cu(2) | 0.830 79(7) | 0.855 77(6) | 0.645 32(6) |
| O(1A) | 0.287 8(4) | 0.460 7(4) | 0.178 0(3) |
| O(2A) | 0.211 4(4) | 0.552 7(3) | −0.023 9(3) |
| O(3A) | 0.248 3(4) | 0.533 8(4) | 0.321 5(3) |
| O(4A) | 0.112 1(4) | 0.681 9(4) | −0.012 1(3) |
| O(1B) | 0.136 4(4) | 0.138 6(4) | 0.195 0(3) |
| O(2B) | 0.281 0(4) | 0.053 2(4) | 0.370 5(4) |
| O(3B) | 0.153 0(4) | 0.078 1(4) | 0.032 5(3) |
| O(4B) | 0.363 4(4) | −0.071 7(4) | 0.315 3(4) |
| O(1V) | 0.095 5(4) | 0.274 8(4) | −0.037 1(3) |
| O(1W) | 0.671 5(4) | 0.666 3(4) | 0.588 1(4) |
| O(1X) | 0.231 9(4) | −0.079 7(4) | −0.082 4(4) |
| O(1Y) | 0.419 3(5) | 0.657 8(5) | 0.526 2(4) |
| O(1Z) | 0.396 9(5) | −0.112 4(5) | 0.547 6(4) |
| N(1) | 0.394 1(4) | 0.329 0(4) | 0.071 5(4) |
| N(2) | 0.332 2(4) | 0.416 2(4) | −0.117 3(4) |
| N(3) | 0.952 0(5) | 0.768 0(4) | 0.643 6(4) |
| N(4) | 0.849 0(5) | 0.880 7(4) | 0.490 8(4) |
| C(1A) | 0.427 2(6) | 0.288 4(5) | 0.170 2(5) |
| C(2A) | 0.498 3(6) | 0.213 9(6) | 0.186 2(5) |
| C(3A) | 0.536 4(6) | 0.173 7(6) | 0.100 7(6) |
| C(4A) | 0.502 0(6) | 0.215 3(5) | −0.004 4(5) |
| C(5A) | 0.537 3(6) | 0.182 7(6) | −0.099 8(6) |
| C(6A) | 0.507 3(6) | 0.229 3(6) | −0.195 5(5) |
| C(7A) | 0.438 6(6) | 0.312 6(6) | −0.206 3(5) |
| C(8A) | 0.404 5(6) | 0.367 8(6) | −0.305 1(5) |
| C(9A) | 0.3393 | 0.441 8(6) | −0.303 7(5) |
| C(10A) | 0.302 5(6) | 0.467 0(6) | −0.211 1(5) |
| C(11A) | 0.399 4(5) | 0.342 2(5) | −0.116 3(5) |
| C(12A) | 0.433 4(5) | 0.293 3(5) | −0.013 0(5) |
| C(13A) | 0.238 1(6) | 0.522 9(5) | 0.220 8(5) |
| C(14A) | 0.161 0(6) | 0.591 3(6) | 0.149 4(5) |
| C(15A) | 0.161 7(6) | 0.609 3(5) | 0.030 2(5) |
| C(1B) | 1.004 7(6) | 0.714 4(6) | 0.726 9(6) |
| C(2B) | 1.085 2(7) | 0.653 7(6) | 0.711 4(6) |
| C(3B) | 1.108 5(7) | 0.642 3(6) | 0.612 1(6) |
| C(4B) | 1.050 8(6) | 0.697 2(5) | 0.521 1(5) |
| C(5B) | 1.067 0(6) | 0.689 7(6) | 0.411 7(5) |
| C(6B) | 1.012 1(6) | 0.745 9(6) | 0.332 5(5) |
| C(7B) | 0.937 6(6) | 0.815 0(5) | 0.354 1(5) |
| C(8B) | 0.883 1(6) | 0.884 0(6) | 0.277 5(5) |
| C(9B) | 0.816 8(7) | 0.947 4(6) | 0.309 8(5) |
| C(10B) | 0.796 9(6) | 0.945 2(6) | 0.415 0(5) |
| C(11B) | 0.917 6(5) | 0.819 5(5) | 0.459 9(5) |
| C(12B) | 0.974 7(6) | 0.758 6(5) | 0.544 3(5) |
| C(13B) | 0.161 3(6) | 0.068 1(5) | 0.131 4(5) |
| C(14B) | 0.201 1(6) | −0.035 7(5) | 0.177 7(5) |
| C(15B) | 0.288 2(6) | −0.017 0(6) | 0.295 1(5) |

**Table 3.** Selected bond lengths and angles for [Cu(phen)(mal)($H_2O$)]·1.5$H_2O$ with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

| | | | |
|---|---|---|---|
| Cu–O(1V) | 2.266(3) | Cu–N(1) | 2.014(4) |
| Cu–O(1A) | 1.909(3) | Cu–N(2) | 2.021(4) |
| Cu–O(2A) | 1.919(3) | | |

(*b*) Bond angles (°)

| | | | |
|---|---|---|---|
| O(1A)–Cu–O(1V) | 98.73(14) | O(2A)–Cu–N(1) | 168.45(15) |
| O(1A)–Cu–O(2A) | 94.82(13) | O(2A)–Cu–N(2) | 92.36(14) |
| O(1A)–Cu–N(1) | 89.55(15) | O(1V)–Cu–N(1) | 95.98(13) |
| O(1A)–Cu–N(2) | 165.04(16) | O(1V)–Cu–N(2) | 93.86(14) |
| O(2A)–Cu–O(1V) | 93.92(13) | N(1)–Cu–N(2) | 81.08(15) |

It is interesting to note that whereas the five-membered chelate ring of phen with copper is essentially planar, the six-membered chelate ring of mal with copper assumes a boat conformation. The Cu and C(14) atoms are displaced by

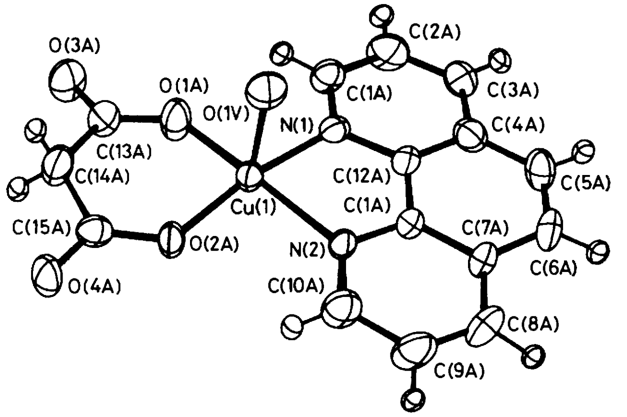

Figure 1. ORTEP drawing of $[Cu(phen)(mal)(H_2O)]\cdot 1.5H_2O$; only O(1V) from water directly bound to Cu(1) is shown

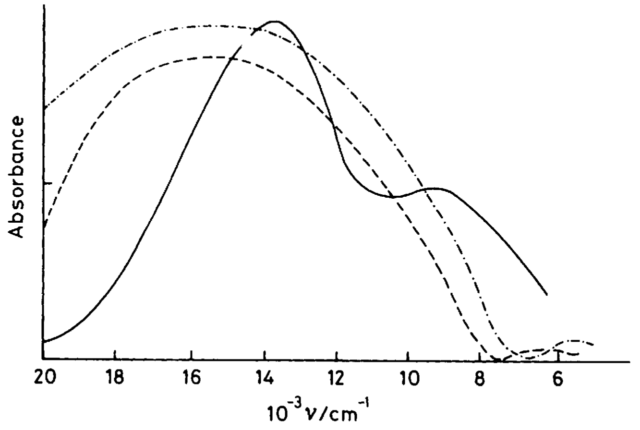

Figure 2. Visible reflectance spectra of (*a*) [Cu(phen)(ox)] (——), (*b*) $[Cu(phen)(mal)(H_2O)]\cdot 1.5H_2O$ (– – – –), (*c*) $[Cu(bipy)(mal)(H_2O)]$ [—′—′—]

Table 4. Cu–O distances (Å) in $Cu^{II}$ malonate complexes

| | |
|---|---|
| $[Cu^{II}(NH_2CH_2CH_2NHMe)(mal)]\cdot H_2O$[a] | 1.956(6), 1.940(6) |
| $[Cu^{II}(NH_2CH_2CH_2CH_2NH_2)(mal)]$[b] | 1.994(7), 1.988(7) |
| $[Cu^{II}\{Me_2C(NH_2)CH_2NHPr^i\}(mal)]\cdot 2H_2O$[c] | 1.952(6), 1.924(6) |
| $[Cu^{II}(EtHNCH_2CH_2NHEt)(mal)(H_2O)]\cdot H_2O$[d] | 1.950(3), 1.950(4) |
| $[Cu^{II}(phen)(mal)(H_2O)]\cdot 1.5H_2O$ | 1.909(3), 1.919(3) |

[a] R. Hamalainen and A. Pajunen, *Finn. Chem. Lett.*, 1973, 284. [b] A. Pajunen and E. Nasakkala, *Finn. Chem. Lett.*, 1977, 100. [c] Ref. 10. [d] Ref. 11.

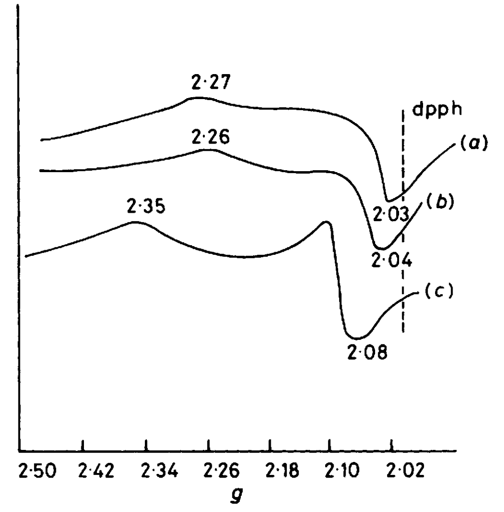

Figure 3. Polycrystalline e.s.r. spectra of (*a*) $[Cu(phen)(mal)(H_2O)]\cdot 1.5H_2O$, (*b*) $[Cu(bipy)(mal)(H_2O)]$, and (*c*) [Cu(phen)(ox)]; dpph = diphenylpicrylhydrazyl

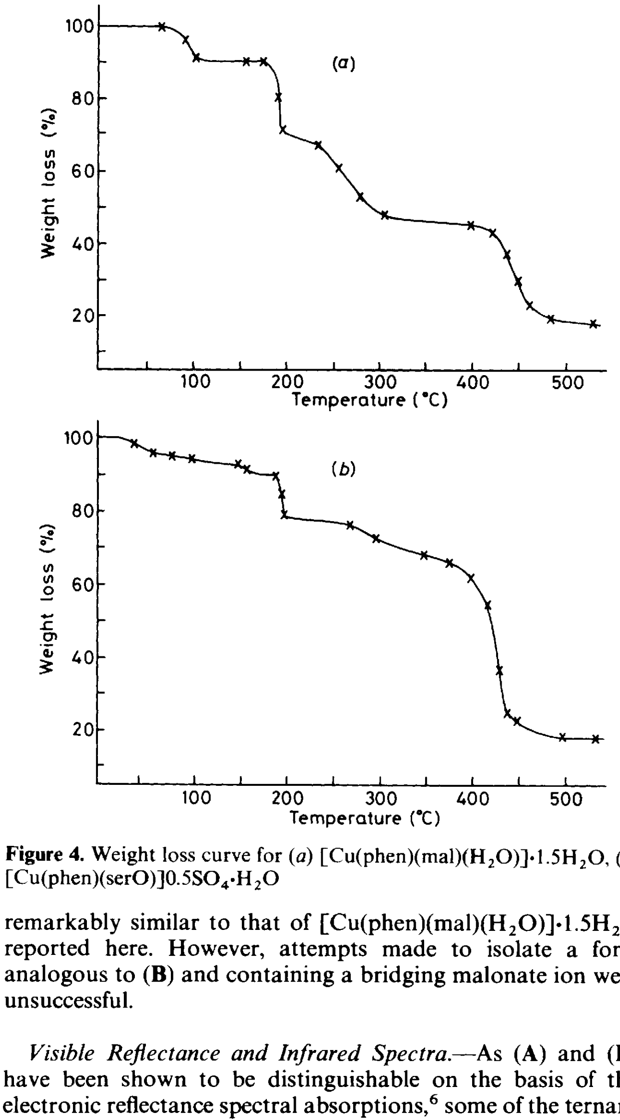

Figure 4. Weight loss curve for (*a*) $[Cu(phen)(mal)(H_2O)]\cdot 1.5H_2O$, (*b*) $[Cu(phen)(serO)]0.5SO_4\cdot H_2O$

+0.189(1) and +0.125(7) Å respectively from the least-squares plane containing O(1), C(13), C(15), and O(2). The phenanthroline is very nearly planar with a dihedral angle of 3.6° between the two pyridine rings.

For the closely related ternary complex of copper(II) containing bipy and oxalate, Hathaway and co-workers[6] have demonstrated in an *X*-ray structural study that there are two forms, *viz.* $[Cu(bipy)(ox)(H_2O)]\cdot 2H_2O$ (**A**) and $[Cu(bipy)(ox)]\cdot 2H_2O$ (**B**). Form (**A**) contains the $CuN_2O_2O'$ chromophore with both bidentate ligands symmetrically co-ordinated. In (**B**), a six-co-ordinate $CuN_2O_2O'_2$ chromophore is found, in which the bipy ligand is symmetrically co-ordinated but the ox is bridging and unsymmetrically co-ordinated. The structure of (**A**) is remarkably similar to that of $[Cu(phen)(mal)(H_2O)]\cdot 1.5H_2O$ reported here. However, attempts made to isolate a form analogous to (**B**) and containing a bridging malonate ion were unsuccessful.

*Visible Reflectance and Infrared Spectra.*—As (**A**) and (**B**) have been shown to be distinguishable on the basis of the electronic reflectance spectral absorptions,[6] some of the ternary complexes of copper(II) we reported earlier[7,8] were re-examined by visible reflectance spectral measurements (Figure 2) over the

**Table 5.** Percentage weight losses at temperature ranges and calculated percentage weight losses of selected groups

| Complex[a] | Temperature range (°C) | Weight loss observed (%) | Group | Calc. weight loss (%) |
|---|---|---|---|---|
| (**1**) [Cu(phen)(ox)] | 180—225 | 18 | $1.5CO_2$ | 18 |
| | 380—400 | 5 | $0.5CO_2$ | 5 |
| | 460—580 | 55 | phen | 54.3 |
| | at 580 | 20[b] | $Cu_2O$ | 19.0 |
| (**2**) [Cu(phen)(mal)($H_2O$)]·$1.5H_2O$ | 65—110 | 10 | $2H_2O$ | 9.43 |
| | 190—196 | 23 | $2CO_2$ | 23.0 |
| | 240—305 | 22 | $CH_2 + C_6H_4$ | 24.0 |
| | 420—500 | 28 | $C_6H_4N_2$ | 28.0 |
| | at 500 | 18[b] | $Cu_2O$ | 19.0 |
| (**3**) [Cu(phen)(suc)($H_2O$)][c] | 80—100 | 5 | $H_2O$ | 4.8 |
| | 200—210 | 24 | $2CO_2$ | 23.3 |
| | 210—250 | 26 | $C_2H_4 + C_6H_4$ | 28 |
| | 350—470 | 27.5 | $C_6H_4N_2$ | 28 |
| | at 490 | 18[b] | $Cu_2O$ | 18.9 |
| (**4**) [Cu(phen)(serO)]$0.5SO_4$·$H_2O$ | 40—80 | 4.5 | $H_2O$ | 4.5 |
| | 140—160 | 4.1 | $NH_3$ | 4.3 |
| | 195—200 | 10.6 | $CO_2$ | 11.0 |
| | 400—500 | 43.5 | phen | 45.4 |
| | at 510 | 17.2[b] | $Cu_2S$ | 18.0 |
| (**5**) [Cu(phen)(alaO)]$0.5SO_4$·$H_2O$ | 40—80 | 4.5 | $H_2O$ | 4.5 |
| | 140—165 | 4.0 | $NH_3$ | 4.3 |
| | 200—210 | 12 | $CO_2$ | 11.0 |
| | 405—490 | 45.4 | phen | 45.4 |
| | at 510 | 19.0[b] | $Cu_2S$ | 21.0 |
| (**6**) [Cu(phen)(tyrO)]Cl·$2H_2O$ | 60—100 | 8.0 | $2H_2O$ | 8 |
| | 140—200 | 15 | $NH_3 + CO_2$ | 14 |
| | 250—380 | 23 | tyrosine residue | |
| | 420—560 | 36.5 | phen | 35 |
| | at 560 | 16[b] | $Cu_2O$ | 15 |

[a] Abbreviations: suc = succinate(2−), serO = serinate(1−), alaO = alaninate(1−), tyrO = tyrosinate(1−). [b] This value corresponds to the calculated weight percentage of the residue. [c] As the structure has not been elucidated, the co-ordinated water is deduced from i.r. data.

range 6 000—25 000 cm$^{-1}$. Although the methanolic solution and Nujol electronic spectra of all these complexes were found[7] to be similar, the electronic reflectance spectra of [Cu(phen)(ox)], [Cu(phen)(mal)($H_2O$)]·$1.5H_2O$, and [Cu(bipy)(mal)($H_2O$)] display an interesting feature. Reflectance spectra of complexes [Cu(phen)(mal)($H_2O$)]·$1.5H_2O$ and [Cu(bipy)(mal)($H_2O$)] contain single broad bands at 15 625 and 15 870 cm$^{-1}$ respectively. These are remarkably similar to that at 15 600 cm$^{-1}$ for (**A**) with the $CuN_2O_2O'$ chromophore.[6] [Cu(phen)(ox)], on the other hand, displays a visible band at 14 500 cm$^{-1}$ and a broad shoulder at *ca.* 9 000 cm$^{-1}$; similar bands were reported[6] for (**B**), having a $CuN_2O_2O'_2$ chromophore and a bridging oxalate ion. It would appear that the oxalate ion has a greater tendency than the malonate ion to bridge copper(II) centres in these ternary complexes. Moreover the $\alpha,\alpha'$-di-imine (phen or bipy) probably has little influence over the dicarboxylate in bridging metal centres. Finally for complexes (**3**)—(**6**) in Table 5 a broad band occurs in the range 15 500—15 800 cm$^{-1}$, indicative of a similar co-ordination geometry as in (**A**).

In the search for another possible indicator to determine the co-ordination mode of carboxylate ion in these complexes, the i.r. bands, particularly the symmetric ($\nu_{sym}$) and antisymmetric ($\nu_{asym}$) stretches of the carboxylate, were compared with values reported for related systems.[8] The separation of these bands was found in each case to be typical of unidentate carboxylate acids (*ca.* 260 cm$^{-1}$).[19] The metal–oxygen stretchings were found to lie within a narrow range (790 ± 10 cm$^{-1}$) comparable to those of other M–O(carboxylate) bonds. Thus although the Cu–O-(carboxylate) distances have been found from the present and other *X*-ray structural studies to vary somewhat, such variation is not manifested in the Cu–O stretches.

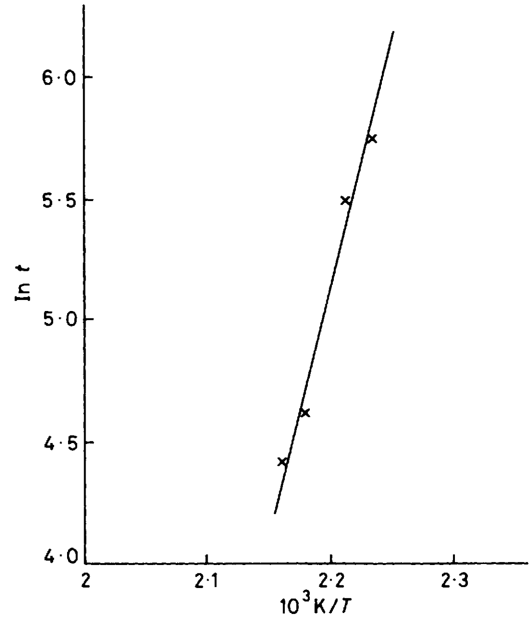

**Figure 5.** Determination of activation energy of [Cu(phen)(mal)($H_2O$)]·$1.5H_2O$ at 30% decomposition; *t* = rate of heating (°C min$^{-1}$)

Finally, as for (**A**) and (**B**), the polycrystalline e.s.r. of [Cu(phen)(mal)($H_2O$)]·$1.5H_2O$, [Cu(bipy)(mal)($H_2O$)], and [Cu(phen)(ox)] are found to be approximately axial, with the value of the high *g* factor for the oxalate being significantly different from those of the two malonate complexes, Figure 3.

*Thermogravimetric Analysis.*—In addition to the complexes $[\mathrm{Cu(phen)(ox)}]$ and $[\mathrm{Cu(phen)(mal)(H_2O)}]\cdot 1.5\mathrm{H_2O}$, several copper(II) complexes containing phen or bipy and a dicarboxylic acid or an amino acid were subjected to t.g.a. Some of the results are summarised in Table 5 and Figure 4(*a*) and (*b*). Thus the plots of percentages of weight loss against temperature indicate that the thermal decomposition of (**2**) and (**3**) proceeded in four steps [Table 5, Figure 4(*a*) and (*b*)] but that of (**4**)—(**6**) proceeded in three steps only. A comparison of these values with the calculated percentage weight losses of $H_2O$, $CO_2$, and $NH_3$ (Table 5) suggests that the steps at *ca.* 100 and *ca.* 200 °C correspond to the removal of $H_2O$ and $CO_2$ respectively, while an additional step at *ca.* 160 °C can be attributed to the loss of $NH_3$ in (**4**)—(**6**). It is interesting to note that the decomposition of phen apparently occurs in two steps for (**2**) and (**3**) but in one single step for (**4**)—(**6**). The calculated percentage weight of the residue in each case suggests that $Cu_2O$ was the final product.

The loss of $H_2O$ molecules in (**2**) (80—100 °C) occurs at a significantly higher temperature than that for the structurally similar (**A**) (65—100 °C). This suggests that the co-ordinated water molecule is held more tightly to the metal centre in (**2**), consistent with the relative magnitude of the Cu–$OH_2$ bond distances of 2.266 and 2.341 Å in (**2**) and (**A**) respectively. The temperature range for the loss of water of crystallisation has been found to be 42—65 °C,[20,21] which is also found for (**4**)—(**6**). That this temperature range has not been observed in (**2**) and (**3**) indicates that strong hydrogen bonding probably exists throughout the crystal lattice.

The t.g.a. behaviour of (**1**) (Table 5) is different from (**2**) and (**3**), both containing a dicarboxylic acid. Thus the observed percentage weight losses at the high temperatures of 220 and 380 °C are the equivalents of 1.5 $CO_2$ and 0.5 $CO_2$ respectively. The higher temperatures of decarboxylation may be due to the presence of a bridging oxalate. However a more affirmative assignment is possible only when *X*-ray structural data become available.

*Activation Energies for Solid-state Reactions of Complexes* (**2**) *and* (**4**).—The activation energy was calculated by isothermal analysis[22] for complexes (**2**) (Figure 5) and (**4**). These were found to be 22.6 kJ mol$^{-1}$ for 10% decomposition corresponding to the loss of two moles of water in complex (**2**) and 55.7 kJ mol$^{-1}$ for 8.6% decomposition corresponding to the release of one mole of water and one mole of ammonia in complex (**4**).

Activation energies for solid-state reactions are scarce but a value of 100 kJ mol$^{-1}$ has been reported[23] to be the activation energy of dehydration for the *cis* isomer of bis(glycinato)-copper(II). However this was determined by differential scanning calorimetry (d.s.c.) and the loss of water molecules was found to occur at a much higher temperature range of 160—195 °C. In addition, the present results were obtained under specified procedural conditions which are most likely to be different from those used by others. As only a powder *X*-ray pattern is available for bis(glycinato)copper(II), no rationalisation of the vastly different activation energies can be suggested. The activation energies calculated for decarboxylation, corresponding to the second step of decomposition at 23% weight loss for complex (**2**) and 10.6% weight loss for complex (**4**), are 174.6 and 133 kJ mol$^{-1}$ respectively. These are comparable to values of activation energy[24] interpreted as due to an intramolecular mechanism such as chelate ring opening. The lower activation energy of decarboxylation for complex (**4**) in comparison to complex (**2**) may be due to (*a*) only one mole of $CO_2$ being cleaved, or (*b*) the chelate ring being already partially open following the loss of ammonia at a lower temperature in (**4**).

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