Magnetic Properties of Polynuclear Complexes. Part III. Alkoxo-bridged Complexes of Copper(II)

By **John E. Andrew, Antony B. Blake,*** and **Louis R. Fraser,** Department of Chemistry, The University, Hull HU6 7RX

The magnetic susceptibilities between 80 and 370 K are reported for the complexes [Cu(pd)(OR)] (R = Me, Et, Pr^n, or PhCH$_2$; pd = pentane-2,4-dionato), [Cu(sal)(OCH$_2$Ph)] (sal = salicylaldehydato), [Cu(hacp)(OR)] hacp = 2′-hydroxyacetophenone; R = Pr^n or Bu^n), and [Cu(hnc)(OR)] (Hhnc = 1-hydroxynaphthalene-2-carbaldehyde; R = Pr^n, Bu^n, or PhCH$_2$), (I)—(X) respectively. The data are interpreted on the assumption that these complexes contain dimeric molecules with bridging alkoxo-groups; the exchange parameters (estimated by curve-fitting with g and J varied) are all negative, the value of $|J|$ being 378, 211, 133, 312, 266, 179, 214, 131, 145, and 174 cm^{-1} for (I)—(X) respectively, where $2|J|$ is the singlet–triplet separation. Some evidence is found that $|J|$ increases with increasing base strength of the chelating anions, but there is no obvious correlation with analogous properties of the alkoxo-groups. The preparation and properties of [Cu(O$_2$CMe)(OMe)] are also reported; its magnetic susceptibility and mass spectrum provide some support for a tetranuclear structure.

ALKOXY-GROUPS are notable for their tendency to behave as bridging ligands in polynuclear complexes, and their physical simplicity and chemical variety make them potentially useful probes for the study of superexchange between magnetic ions. Several complexes believed to contain bridging alkoxo-ligands have been found to show spin–spin coupling, *e.g.* [MCl$_2$(OMe)]·2MeOH (M = V or Cr),[1] [Fe(pd)$_2$(OR)] (R = Me, Et, or Pr; pd = pentane-2,4-dionato),[2] [Cu(2-NH$_2$py)(OR)]$^+$ (R = H, Me, Et, Pr, or pentyl; 2-NH$_2$py = 2-aminopyridine),[3] and [Cu(pd)(OMe)].[4,5] The last complex has been assigned a dimeric structure on the basis of its molecular weight in solution,[4] and its magnetic behaviour has been shown to be approximately that expected for a binuclear complex with a rather strong antiferromagnetic exchange interaction.[5] When this complex is recrystallised from a higher alcohol ROH the methoxo-group is replaced by OR, and by starting with the appropriate complex [CuL$_2$] (L = pd or an analogous β-diketonato-ligand) a variety of complexes of the type [CuL(OR)] can be obtained. We report here the results of a magnetic investigation of 10 such complexes (Table 1). The crystal structure of one of them, [Cu(pd)(OCH$_2$Ph)], has recently been determined.[6] Since this work was completed, a magnetic investigation of three of the complexes [Cu(pd)(OR)] (R = Me, Et, and PhCH$_2$) has also been reported by other workers.[5b] We also describe the complex [Cu(O$_2$CMe)(OMe)] obtained by heating copper(II) acetate under reflux with sodium hydroxide in methanol.

TABLE 1

Complexes [CuL(OR)] and some magnetic parameters

Number	L	R	$\mu_{eff.}$(298 K) [a] / B.M.	g [b]	$-J$ [b] / cm^{-1}	10^2R [c]
(I)	pd	Me	0.69	2.59	378	1.4
(II)	pd	Et	1.16	2.18	211	0.7
(III)	pd	Pr^n	1.29	1.90	133	3.6
(IV)	pd	PhCH$_2$	0.83	2.30	312	4.9
(V)	sal	PhCH$_2$	1.05	2.45	266	5.3
(VI)	hacp	Pr^n	1.27	2.13	179	3.4
(VII)	hacp	Bu^n	1.14	2.17	214	3.3
(VIII)	hnc	Pr^n	1.38	2.01	131	5.4
(IX)	hnc	Bu^n	1.32	2.02	145	4.8
(X)	hnc	PhCH$_2$	1.21	2.01	174	1.1
(XI)	MeCO$_2$	Me	0.69 [d]	2.01 [d]	318 [d]	7.7

[a] 1 B.M. ≈ 9.27×10^{-24} A m^2. [b] Values of the parameters in equation (1) which give the best fit to the data. [c] Discrepancy index defined in the text. [d] Based on the assumption that the complex contains 2% Cu[OH]$_2$ impurity by weight.

EXPERIMENTAL

Preparations.—[CuL(OR)].—The complex [CuL$_2$] [7] was converted into [CuL(OMe)] by treatment with sodium hydroxide in refluxing methanol,[4] and the methoxide was then converted into the desired alkoxide by recrystallisation from the appropriate alcohol. (In the case of benzyl alcohol the temperature must be kept below 150 °C to avoid reduction of the complex to metallic copper.) The pentane-2,4-dionato-complexes are blue, and those of the aromatic β-diketonate ligands green, like the corresponding [CuL$_2$]. They all decompose slowly when exposed to the atmosphere.

[Cu(O$_2$CMe)(OMe)]. Sodium hydroxide (0.4 g, 0.01 mol) dissolved in methanol was added dropwise to a refluxing solution of Cu[O$_2$CMe]$_2$·H$_2$O (2.0 g, 0.005 mol) in methanol. The royal blue, microcrystalline precipitate was insoluble in the common organic solvents, and could not be recrystallised.

Analyses.—Microanalysis for C and H was made commercially. Copper was determined gravimetrically as [Cu(en)$_2$][HgI$_4$] (en = ethylenediamine), or as CuF$_2$ after heating in a stream of fluorine and cooling under nitrogen. Analytical results are collected in Table 2.

Physical Measurements.—Magnetic susceptibilities were measured on finely powdered samples by the Gouy method at a number of temperatures between 80 and 350 K. I.r. spectra of pressed KCl discs and Nujol mulls were obtained with Perkin-Elmer PE457 and Unicam SP 200 instruments. Mass spectra were obtained with an A.E.I. MS902 spectrometer. E.s.r. spectra at 9.4 GHz were kindly measured by W. S. Buchan in the Physics Department of this University.

---

[1] L. Dubicki, G. A. Kakos, and G. Winter, *Austral. J. Chem.*, 1968, **21**, 1461; G. A. Kakos and G. Winter, *ibid.*, 1970, **23**, 15.

[2] C. S. Wu, G. R. Rossman, H. B. Gray, G. S. Hammond, and H. J. Schugar, *Inorg. Chem.*, 1972, **11**, 990.

[3] W. R. McWhinnie, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1063.

[4] J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, 1965, **4**, 1657.

[5] (*a*) R. W. Adams, C. G. Barraclough, R. L. Martin, and G. Winter, *Austral. J. Chem.*, 1967, **20**, 2351; (*b*) C. G. Barraclough, R. W. Brookes, and R. L. Martin, *ibid.*, 1974, **27**, 1843.

[6] J. E. Andrew and A. B. Blake, *J.C.S. Dalton*, 1973, 1102.

[7] D. P. Graddon and G. M. Mockler, *Austral. J. Chem.*, 1968, **21**, 617.

RESULTS

Structures of the Complexes.—The complex [Cu(pd)(OCH$_2$Ph)] exists in the crystal as tetrameric molecules with the centrosymmetric structure shown in Figure 1, consisting of two approximately planar dimeric halves held together by relatively long axial Cu–O bonds.[6] Difficulty in obtaining suitable single crystals hindered our attempts to determine the crystal structures of other members of the series, but they presumably contain analogous dimeric molecules, and it seems likely that these dimers are also associated in some way in the solids, although not necessarily as in Figure 1. Mass spectrometry provides some support for this belief, in that peaks corresponding to the ions [Cu$_3$(pd)$_2$(OEt)$_2$]$^+$, [Cu$_3$(pd)$_2$(OPr)]$^+$, and [Cu$_3$(pd)$_3$(OR)]$^+$ (R = Pr or PhCH$_2$) were observed in the spectra of the appropriate complexes, as well as several peaks corresponding to binuclear ions. (The number of Cu atoms was confirmed in each case by the isotope pattern.) These observations must, of course, be treated with caution, since it is possible that the Cu$_3$ fragments were produced from simpler species by reactions in the spectrometer. No Cu$_4$ fragments were positively identified, even in the case of tetrameric [Cu(pd)(OCH$_2$Ph)], and the spectrum of [Cu(pd)(OMe)] gave no evidence for ions containing more than two Cu atoms (perhaps because of the higher temperature required to volatilise this complex). The complexes of aromatic β-diketonate ligands did not give satisfactory mass spectra.

TABLE 2

Elemental analysis (%) of the complex

	Found			Calc.		
Number	C	H	Cu	C	H	Cu
(I)	37.0	5.1	33.5	37.2	5.2	32.9
(II)	40.1	5.6	30.7	40.5	5.8	30.6
(III)	43.3	6.3		43.4	6.3	
(IV)	52.7	5.3		53.5	5.2	
(V)	58.2	4.2		57.6	4.2	
(VI)	51.5	5.4		51.3	5.5	
(VII)	52.5	5.9		53.0	5.9	
(VIII)	56.7	4.5		57.3	4.8	
(IX)	58.6	5.0		58.5	5.2	
(X)	62.9	4.2		63.4	3.8	
(XI)	22.9	4.1	41.8	23.4	3.9	41.4

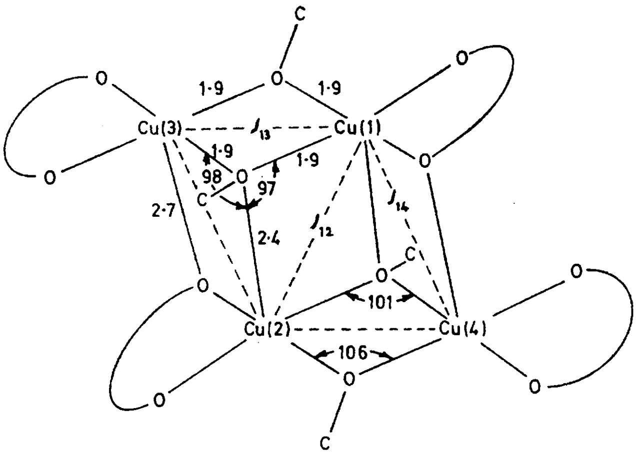
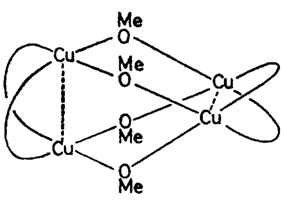


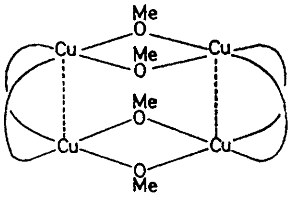
FIGURE 1 Structure of [Cu(pd)(OCH$_2$Ph)], (IV), with pd skeletons indicated by loops. Distances are in Å

The i.r. spectra of the complexes were similar to those of [CuL$_2$] with the addition of bands characteristic of OR, including one or more in the 950—1 120 cm^{-1} region assigned to C–O stretching vibrations. In this they resemble the spectra of [Fe(pd)$_2$(OR)].[2] The complex [Cu(pd)(OMe)] showed a single ν(C–O) band at 1 068 cm^{-1}; the band at *ca.* 1 020 cm^{-1} assigned to the methoxo-group by Bertrand and Kaplan [4] is also present in [Cu(pd)$_2$].

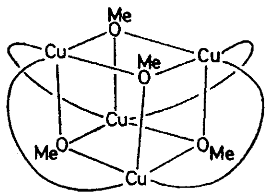
The complex [Cu(O$_2$CMe)(OMe)], though rather involatile, also gave a mass spectrum, in which *m/e* peaks were observed corresponding to the ions [Cu$_4$(O$_2$CMe)$_4$(OMe)$_n$]$^+$ (n = 1—3), [Cu$_4$(O$_2$CMe)$_3$]$^+$, and several trinuclear and binuclear fragments. The most abundant ion was [Cu$_2$(O$_2$CMe)$_2$]$^+$, a fact which suggests that the structure contains these units linked by methoxo-groups, perhaps into tetrameric molecules (which may themselves be further associated by weak Cu–O interactions, as are the dimers in Figure 1). The appearance of Cu$_4$ fragments suggests that the dimeric units are held together more strongly than in [Cu(pd)(OCH$_2$Ph)]. Three possible structures are shown below [(A)—(C); bridging acetate groups are indicated by curved lines].



(A)



(B)



(C)

Magnetic Properties.—The magnetic susceptibilities of the 11 complexes between 80 and 370 K are listed in Supplementary Publication No. SUP 21678 (5 pp.),* and plotted against temperature in Figures 2 and 3. The susceptibilities were corrected for diamagnetism by means of Pascal's constants,[8] and for an assumed temperature-independent paramagnetism (t.i.p.) of 0.75 mm^3 per mol Cu.

Complex (I) was also studied magnetically, over a somewhat wider temperature range, by Adams *et al.*,[5] who reported susceptibility values significantly higher than ours, especially at lower temperatures (*e.g.* χ per monomer, including t.i.p., *ca.* 340 × 10^{-6} at 300 and 230 × 10^{-6} cm^3 mol^{-1} at 230 K,† compared with our values of 267 × 10^{-6} and 145 × 10^{-6} cm^3 mol^{-1} at these temperatures). The levelling off in χ below 200 K led them to attribute an unusually large value to the t.i.p. However, the difference

---

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Articles less than 10 pp. are supplied as full-size copies.)

† We estimated these values from Figure 1 of ref. 5*a*, but Adams *et al.* also mention an uncorrected susceptibility of 220 × 10^{-6} cm^3 mol^{-1} at 298 K. We do not understand the apparent discrepancy, unless they assumed an unusually large diamagnetic correction.

[8] B. N. Figgis and J. Lewis in 'Modern Co-ordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, ch. 6.

between their data and ours could be explained if their sample contained *ca.* 3% of $Cu[OH]_2$,[9] and this would also account for the low carbon content (36.3%) reported for their sample. (Barraclough *et al.*,[5b] in a more recent study of this complex, were led to a similar conclusion.) It is to be noted that, in spite of the disagreement of the absolute susceptibilities, the exchange splitting $2|J|$ which they estimate, 725 cm^{-1}, agrees quite well with ours (see below).

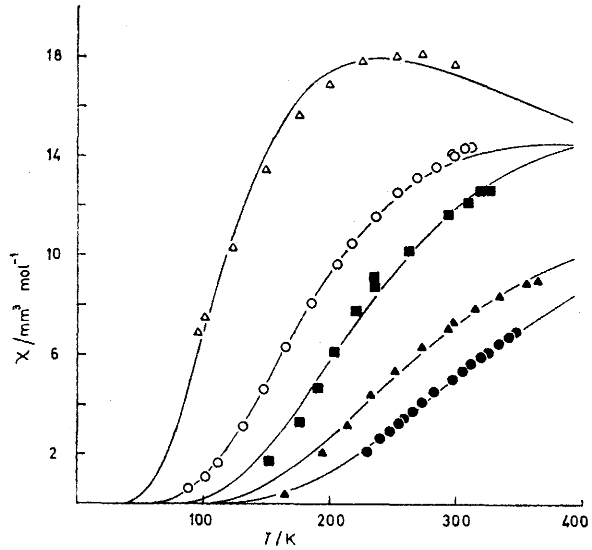


FIGURE 2 Magnetic susceptibilities (per mole of dimer) of complexes (I) (●), (II) (○), (III) (△), (IV) (▲), and (V) (■). The curves were calculated from equation (1), using the *g* and *J* values of Table 1

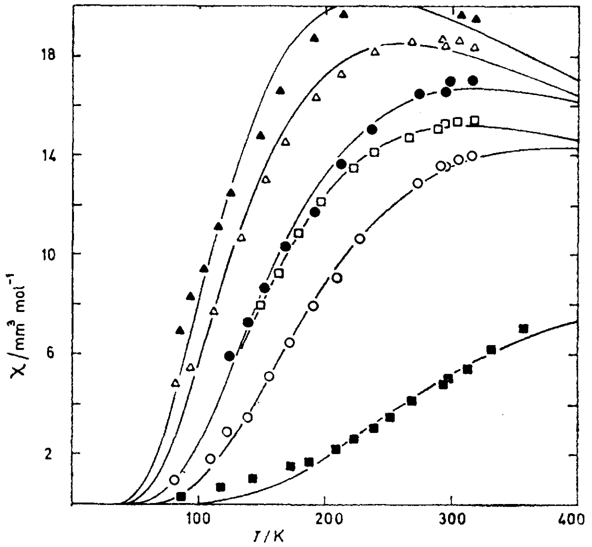


FIGURE 3 Magnetic susceptibilities of complexes (VI) (●), (VII) (○), (VIII) (▲), (IX) (△), (X) (□), and (XI) (■). The data for (XI) were corrected for paramagnetic impurity as described in the text

The susceptibility of $[Cu(O_2CMe)(OMe)]$, (XI), decreased rapidly below 360 K, but levelled off to a relatively high and almost constant value between 140 and 80 K. This behaviour closely resembles that reported by Adams *et al.* for [Cu(pd)(OMe)], and we are inclined to attribute it here also to the presence of a trace amount of $Cu[OH]_2$ which could well have been formed during the preparation, and would not have been removed in this case because the complex is too insoluble to be recrystallised. The analytical results for C and Cu are consistent with the presence of 1—3% of $Cu[OH]_2$, while if we assume that the residual paramagnetism of the sample at 85 K (after correcting for t.i.p.) is entirely due to $Cu[OH]_2$, *ca.* 2% of the latter is indicated. We therefore corrected our data on this assumption for the purpose of estimating *J* values. The results must, of course, be regarded as only approximate. The possibility of paramagnetic impurities is less for complexes (I)—(X), but cannot be entirely ruled out. Deviations of the t.i.p. from the fixed value assumed may also affect the accuracy of the results.

DISCUSSION

Complexes (I)—(X).—Since these complexes almost certainly contain dimeric units [perhaps further associated, as in complex (IV)], we begin by assuming that the spins of the Cu^{2+} ions are coupled in pairs by a Heisenberg exchange operator $-2J\mathbf{S}_1\mathbf{S}_2$. The molar susceptibility of such a pair is given by equation (1), and by

$$\chi_M = 2N\mu_0\mu_B{}^2g^2[kT(e^{-2J/kT} + 3)]^{-1} \qquad (1)$$

fitting this to the experimental data by the method of least-squares we obtain the estimated values of *g* and *J* shown in Table 1. The values of $R = [\Sigma(\chi_{obs.} - \chi_{calc.})^2/\Sigma\chi^2_{obs.}]^{\frac{1}{2}}$ are also listed as a measure of the discrepancy between theory and observation.

The *g* values that result from the curve-fitting process are normal except in the cases of complexes (I), (IV), and (V), for which the values seem unreasonably high, and (III) for which a value of less than 2 is obtained. The e.s.r. spectra of complexes (I)—(X) were measured at room temperature on the powders, and the observed *g* values were between 2.05 and 2.11 (although the spectra were weak and in some cases very anisotropic). We attribute the anomalous values obtained by fitting equation (1) to the data mainly to the existence of exchange interactions other than those within the supposed dimers.

The *J* values from equation (1) are all negative (antiferromagnetic), but they vary widely. In view of our ignorance of the precise structures of the complexes, the accuracy of these estimated values (ostensibly representing exchange wholly within the dimeric unit) is rather uncertain, and indeed the absolute values may be in error by as much as 10—20%. If the structures are sufficiently similar, however, we should expect the relative *J* values to reflect in some way the electronic properties of the ligands. The data are too limited to allow a full analysis of the effects of varying the chelating and the bridging alkoxo-group, but some possible trends can be discerned.

For a given alkoxo-group, $|J|$ seems to decrease in the

---

[9] P. Escoffier and J. Gauthier, *Compt. rend.*, 1961, **252**, 271.

order hacp > pd > sal > hnc,* which is also the order of decreasing base strength of the ligand anion.[10] (The orders hacp > pd, pd > sal, and sal > hnc are each based on only one pair of complexes, but hacp > hnc is found with both Pr^n and Bu^n, and pd > hnc with both Pr^n and benzyl.)

For a given chelating ligand, $|J|$ seems to decrease in the order $Me > PhCH_2 > Et > Bu^n > Pr^n$. (Again, the data are too incomplete to establish the order with any certainty, although $PhCH_2 > Pr^n$ and $Bu^n > Pr^n$ are each observed with two different ligands.) This sequence does not seem to be related to properties such as Hammett σ constants, and also contrasts with the variation in room-temperature magnetic moments in the series $[\{Cu(2\text{-}NH_2py)_2(OR)\}_2][NO_3]_2$ studied by McWhinnie,[3] which suggested that superexchange decreased in the order $Et > Me > Pr^n >$ pentyl > H.

Thus, although there is some indication that the strength of exchange varies inversely with the extent of electron transfer from the chelating ligand to copper, the inductive properties of the group R have at most a secondary effect on J, and we attribute most of the variation of J with R to structural changes. (The effect of the chelating ligand would probably be relatively independent of such changes.) Little more can be said about complexes (I)—(III) and (V)—(X) until their detailed structures are known.

Complex (XI).—The structure of this complex is unfortunately not known, and there are grounds for suspecting that our preparation contains a magnetically significant amount of paramagnetic impurity (although measurements at lower temperatures than we could attain would be necessary to be sure of this). We tried to fit both the uncorrected magnetic data, and those in which allowance was made for 2% of $Cu[OH]_2$ as an impurity, to various reasonable models, but the results are rather inconclusive. With the uncorrected data, the theoretical expressions for a binuclear structure and for tetranuclear structures of symmetry D_{2h}, D_{2d}, or T_d [Appendix, equation (A.2)] gave a very poor fit ($R > 0.2$) or an unacceptable g value (<1.6) or both. The corrected data could be fitted reasonably well by any of these expressions, but when we assumed a reasonable value of 2.1 for g, the structure that agreed best with the data was rectangular with J_1 *ca.* -350, J_2 *ca.* $+300$, and J_3 *ca.* $+30$ cm^{-1} (R *ca.* 0.06). The D_{2d} model gave poorer agreement (R *ca.* 0.1) over a wide range of the two exchange parameters, with no unique best fit.

It is interesting to note the analogy between the complexes $[Cu(pd)(OR)]$ and $[Cu(O_2CMe)(OMe)]$ on the one hand, and $[Fe(pd)_2(OR)]$ and $[Fe(O_2CMe)(OMe)_2]$ on the other. The complex $[Fe(pd)_2(OEt)]$ has been found to be dimeric in solution,[2,†] whereas iron(III) alkanoate methoxides are insoluble, and their magnetic behaviour is fitted best by a tetrameric model with the Fe atoms at the corners of a square [11] (although it must be borne in mind that the effect of exchange in a square cluster cannot be distinguished magnetically from that in one of D_{2d} symmetry).

APPENDIX

The susceptibility of a rectangular cluster of four $S = \frac{1}{2}$ spin-only ions in the presence of the exchange Hamiltonian (A.1) is given by equation (A.2), where $x = \exp[(J_1 + J_2 + J_3)/\boldsymbol{k}T]$, y_i $(i = 1\text{—}3) = \exp\,[-(J_1 + J_2 + J_3) + 2J_i\boldsymbol{k}T$, z_i $(i = 1 \text{ or } 2) = \exp\,[-(J_1 + J_2 + J_3) \pm 2D]/\boldsymbol{k}T$, and $D = J_1^2 + J_2^2 + J_3^2 - J_1J_2 - J_2J_3 - J_3J_1$. The susceptibility of a tetranuclear cluster of symmetry D_{2d} or D_{4h} is obtained from (A.2) by setting $J_2 = J_3$. The expression for a tetrahedron results when all three exchange parameters are equal.

$$\mathscr{H} = -2[J_1(\mathbf{S}_2\mathbf{S}_1 + \mathbf{S}_3\mathbf{S}_4) + J_2(\mathbf{S}_2\mathbf{S}_3 + \mathbf{S}_1\mathbf{S}_4) + J_3(\mathbf{S}_1\mathbf{S}_3 + \mathbf{S}_2\mathbf{S}_4)] \quad \text{(A.1)}$$

$$\chi_M = \frac{N\mu_B^2g^2}{\boldsymbol{k}T}\,\frac{10x + 2(y_1 + y_2 + y_3)}{5x + 3(y_1 + y_2 + y_3) + z_1 + z_2} \quad \text{(A.2)}$$

We thank the University of Hull and the S.R.C. for studentships. Computing was done at the Centre for Computer Studies, University of Hull.

[4/1200 *Received*, 19*th June*, 1974]

---

* hacp = 2′-hydroxyacetophenone, Hhnc = 1-hydroxynaphthalene-2-carbaldehyde.

† The complex $[Fe(pd)_2(OMe)]$ has apparently not been prepared, but $[Fe(pd)(OMe)_2]$ is known; it is insoluble and presumably polymeric.[12]

[10] 'Stability Constants of Metal-Ion Complexes,' Special Publ. Nos. 17 and 25, The Chemical Society, London, 1964 and 1971.

[11] E. Kokot, G. M. Mockler, and G. L. Sefton, *Austral. J. Chem.*, 1973, **26**, 2105.

[12] E. Kokot, G. M. Mockler, and G. L. Sefton, *Austral. J. Chem.*, 1973, **26**, 875.