Notes

Dicopper(II) Complexes of an N_6O_2 Macrocycle and Seven-co-ordinate Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Complexes of its N_5O_2 Open-chain Precursor †

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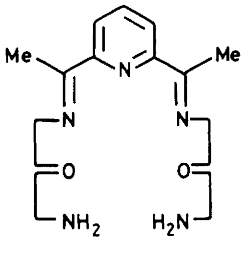
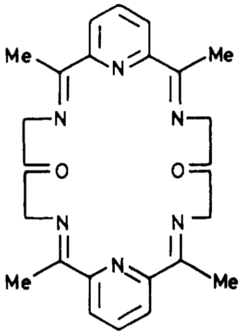
The syntheses, *via* metal-ion (Mg^{2+}, Ca^{2+}, or Ba^{2+}) template methods followed by transmetallation, of the complexes $[ML^1]X_2$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II}; X = ClO_4^- or BPh_4^-) of the potentially septidentate ligand L^1 formed by condensation of 1 mol of 2,6-diacetylpyridine with 2 mol of 3-oxapentane-1,5-diamine is described. The collective evidence of the properties (magnetic and spectroscopic) of the complexes indicates a seven-co-ordinate (pentagonal-bipyramidal) structure. Ring closure, *via* a transamination mechanism, of L^1 in $BaL^1(ClO_4)_2$ leads to the complex $BaL^2(ClO_4)_2 \cdot 3H_2O$ containing the 24-membered N_6O_2 macrocyclic ligand L^2. The single Ba^{2+} in this complex may be replaced by two copper(II) ions to afford the binuclear complex $Cu_2L^2(ClO_4)_4 \cdot H_2O$ which on treatment with imidazole (Him) gives $Cu_2L^2(im)(ClO_4)_3 \cdot H_2O$ containing an imidazolate bridge between the antiferromagnetically coupled metal centres.

Earlier papers [1-5] have described how certain non-transition metal ions may be used to control the course of condensation reactions between dicarbonyl compounds and di-primary amines so as to lead to complexes of macrocyclic Schiff-base ligands in moderate to high yield. It was shown that, under mild reaction conditions, complexes of open-chain intermediates derived from the condensation of one molecule of diketone with two molecules of diamine could be isolated and that these could subsequently undergo ring closure *via* transamination to the [2 + 2] macrocycle.[1-3] We here report an extension of this synthetic strategy to the stepwise synthesis of the new 24-membered N_6O_2 macrocyclic ligand L^2 which has a binucleating capability towards Cu^{II}. Also described are a series of seven-co-ordinate complexes of the metal ions Mn^{II} to Zn^{II} of a septidentate open-chain intermediate L^1 in the macrocycle synthesis.



L^1



L^2

Results and Discussion

Template Synthesis of L^1 *and* L^2.—Reaction of 2,6-diacetylpyridine with 3-oxapentane-1,5-diamine in 1 : 2 molar proportions in methanol in the presence of one equivalent of the perchlorate salt of Mg^{II}, Ca^{II}, or Ba^{II} afforded crystalline complexes $ML^1(ClO_4)_2$ of the potentially septidentate ligand L^1 in 20—60% yield. Analytical and i.r. data (Table 1) established the nature of the Schiff-base ligand L^1 in these complexes. Relevant features of the i.r. spectra are a strong doublet at *ca.* 3 350, 3 310 cm^{-1} [assigned to $\nu(NH_2)$], a moderately intense band at *ca.* 1 590 cm^{-1} [$\delta(NH_2)$], a strong band at *ca.* 1 640 [ν(C=N)], together with absorptions characteristic of co-ordinated pyridine. No carbonyl bands were apparent in any of the spectra. As judged by the unsplit nature of the ClO_4^- vibrations occurring at *ca.* 1 090 and 625 cm^{-1} these anions appear not to be co-ordinated. The complexes therefore probably have seven-co-ordinate structures (see later). They are uni-bivalent electrolytes in MeCN solution (Table 1).

Heating $BaL^1(ClO_4)_2$, but not the corresponding complex of Mg^{II} or Ca^{II}, in dry MeOH to *ca.* 60 °C for 1 h afforded the complex $BaL^2(ClO_4)_2 \cdot 3H_2O$ in 35—40% yield. Somewhat higher yields were obtained if an equivalent of 2,6-diacetylpyridine was added at the start of the reaction. I.r. spectra (Table 1) indicated the presence of the macrocycle L^2 in this complex [intensification of the ν(C=N) vibration at 1 630 cm^{-1}, and absence of $\nu(NH_2)$ and $\delta(NH_2)$ absorptions]. The occurrence of the ring closure to the [2 + 2] macrocycle L^2 is consistent with a transamination mechanism involving a sequence of intermolecular and intramolecular nucleophilic additions (followed by deamination) of NH_2 groups at co-ordinated C=N centres, as shown previously for related systems.[1-3]

The alkaline-earth-metal ion complexes of both the open-chain ligand L^1 and the macrocyclic ligand L^2 are useful precursors to a range of seven-co-ordinate transition-metal complexes of L^1 and to dicopper(II) complexes of L^2 as described below. None of the transition-metal complexes (of either ligand) could be prepared by a direct synthetic route which by-passed the use of the alkaline-earth-metal ion.

Seven-co-ordinate Metal(II) *Complexes of* L^1.—Treatment of $ML^1(ClO_4)_2$ (M = Mg^{II}, Ca^{II}, or Ba^{II}; best results obtained with Ca^{II}) in MeOH with $M(ClO_4)_2 \cdot 6H_2O$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II}) at 30 °C gave crystals of the product complexes $[ML^1][ClO_4]_2$ in 70—80% yield. The tetraphenyl-

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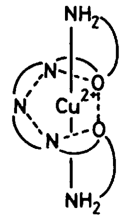
† *Non-S.I. units employed:* B.M. ≈ 9.27×10^{-24} A m^2; G = 10^{-4} T; mmHg ≈ 134 Pa; $\chi_{c.g.s.} = 4\pi \times 10^{-6}$ S.I. unit.

Table 1. Analytical, i.r., magnetic, and electrical conductance data for the complexes

	Analysis (%)						I.r. bands/cm^{-1}		$\mu_{eff.}$[a]/ B.M.	Λ[b]/ S cm^2 mol^{-1}
	Found			Calc.						
Complex	C	H	N	C	H	N	ν(NH_2)	ν(C=N)		
$MgL^1(ClO_4)_2$	36.6	5.4	12.0	36.6	5.2	12.5	3 320, 3 270	1 648		306
$CaL^1(ClO_4)_2$	35.5	5.2	11.7	35.6	5.2	12.2	3 345, 3 290	1 648		294
$BaL^1(ClO_4)_2$	30.1	4.4	10.1	30.4	4.4	10.4	3 358, 3 295	1 636		285
$BaL^2(ClO_4)_2\cdot 3H_2O$	36.3	4.4	9.4	36.6	4.7	9.8		1 630		263
$[MnL^1][ClO_4]_2$	34.5	4.7	11.9	34.7	4.9	11.9	3 325, 3 275	1 640	5.88	
$[MnL^1][BPh_4]_2$	76.0	6.9	6.8	75.9	6.4	6.8	3 285, 3 240	1 635	5.89	
$[FeL^1][ClO_4]_2$	34.5	5.0	11.6	34.6	5.0	11.8	3 320, 3 273	1 633	5.17	294
$[FeL^1][BPh_4]_2$	75.7	6.8	6.7	75.8	6.8	6.8	3 288, 3 242	1 624	5.21	243
$[CoL^1][ClO_4]_2$	34.4	5.0	11.7	34.4	4.9	11.8	3 320, 3 275	1 639	4.31	278
$[CoL^1][BPh_4]_2$	75.7	6.9	6.8	75.6	6.7	6.8	3 300, 3 250	1 635	4.45	239
$[NiL^1][ClO_4]_2$	34.1	5.0	11.3	34.4	4.9	11.8	3 310, 3 268	1 632	3.14	285
$[NiL^1][BPh_4]_2$	75.7	6.9	6.8	75.6	6.7	6.8	3 295, 3 243	1 629	3.21	242
$[CuL^1][ClO_4]_2$	34.1	4.7	11.6	34.1	4.9	11.7	3 300, 3 260	1 635	1.89	292
$[CuL^1][BPh_4]_2$	75.0	6.8	6.7	75.3	6.7	6.8	3 280, 3 235	1 630	1.84	
$[ZnL^1][ClO_4]_2$	33.8	4.9	11.7	34.0	4.9	11.7	3 310, 3 260	1 642		
$[ZnL^1][BPh_4]_2$	74.2	6.5	6.4	75.1	6.7	6.7	3 290, 3 240	1 638		
$Cu_2L^2(ClO_4)_4\cdot H_2O$	31.6	3.7	8.8	31.1	3.6	8.4		1 625	1.90 (1.84)	374
$Cu_2L^2(im)(ClO_4)_3\cdot H_2O$	35.6	3.9	11.3	35.8	4.0	11.5		1 628	1.85 (1.66)	330

[a] Magnetic moment per metal atom at 293 K corrected for diamagnetism of ligands; values in parentheses refer to 93 K. [b] For 10^{-3} mol dm^{-3} solutions in MeCN at 20 °C.



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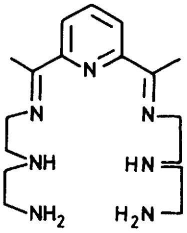

L^3

borate salts were obtained in high yield by metathesis. Analytical and other physical data are in Table 1. The i.r. spectra are virtually identical, being independent of the nature of the metal ion. They show the expected features of the L^1 ligand *viz.* ν(C=N), ν(NH_2), δ(NH_2), co-ordinated pyridine, ionic ClO_4^-, and, in the case of $[BPh_4]^-$ salts, ν(C–O–C) at *ca.* 1 085 cm^{-1}, *i.e.* at an energy significantly lower than in the free ether (1 118 cm^{-1}) indicating ether oxygen co-ordination in the complexes. On the assumption that all seven donor atoms are co-ordinated, molecular models indicated that the probable structure for the $[ML^1]^{2+}$ cations is pentagonal bipyramidal with the trimethine N_3 donor set together with the two oxygen donors comprising the equatorial plane, the two axial positions being occupied by the primary amine groups [structure (1)]. This is the arrangement previously found,[4] and confirmed by *X*-ray crystallography in the case of a copper(II) complex, in corresponding complexes of the closely related ligand L^3 in which secondary amine groups take the place of the ether groups of L^1. The assignment of an approximate pentagonal-bipyramidal structure to the L^1 complexes is strongly supported by the collective evidence of the physical properties summarised below.

The room-temperature magnetic moments (Table 1) observed for the complexes of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} show that the metal ions are high-spin with $S = \frac{5}{2}, 2, \frac{3}{2}, 1$, and $\frac{1}{2}$ ground states, respectively. While the observed values of $\mu_{eff.}$ do not allow a distinction to be made between the pentagonal-bipyramidal and high-spin octahedral configurations for most of these metal ions, the values (4.3—4.5 B.M.) obtained for the cobalt(II) complexes are consistent with an orbitally degenerate ground state, as required for D_{5h} symmetry, and inconsistent with a triply degenerate ground state, as required for O_h symmetry.

The Mössbauer spectra of the two iron(II) complexes confirm the high-spin nature of the metal ion. The isomer shifts (relative to iron foil) for the perchlorate complex at 293 and 77 K are, respectively, 0.97 and 1.09 mm s^{-1} (0.98 mm s^{-1} at 293 K for the $[BPh_4]^-$ salt) while the quadrupole splittings are 2.99 and 3.31 mm s^{-1} respectively, at the same two temperatures (2.94 mm s^{-1} at 293 K for the $[BPh_4]^-$ salt). The values of these parameters are very close to those observed for the iron(II) complexes of the related ligand L^3 previously shown to have pentagonal-bipyramidal structures.[4]

The room-temperature e.s.r. powder spectrum of $[CuL^1][BPh_4]_2$ was measured at *X*-band frequency. The axial spectrum with $g_\perp > g_\parallel$ (Figure) is of the type predicted for an axially compressed (d_{z^2} ground state) pentagonal-bipyramidal structure as verified crystallographically for the related complex $[CuL^3][BPh_4]_2$. Values of the derived spectroscopic parameters are $g_\parallel = 2.03$, $g_\perp = 2.20$, and $A_\parallel = 132$ G; $A_\perp$ was not resolved.

Electronic spectra were recorded in the range 25 000—5 000 cm^{-1} in the solid state and in MeCN solution. Fair correspondence of the spectra in the two phases was observed. The spectra of the iron(II) complexes are dominated by an intense $(d_{xz},d_{yz}) \rightarrow p_\pi^*$ metal-to-ligand charge-transfer band occurring at 16 200 cm^{-1}, *i.e.* at a slightly higher energy than found[4] for $[FeL^3][ClO_4]_2$, and no ligand-field bands were resolved. The spectra of the complexes of Co^{II} and Ni^{II} are again very similar to those of the previously characterised[4] pentagonal-bipyramidal complexes of L^3, and clearly different from typical spectra of these ions in more common stereochemical environments. A useful diagnostic feature of Ni^{II} in D_{5h} symmetry appears to be the occurrence of a low-energy band at 6 500—7 000 cm^{-1}. The two bands at 11 900 and 7 400 cm^{-1} in the spectra of the copper(II) complexes are assigned to the transitions $^2A_1' \longrightarrow {}^2E_1''$ and $^2A_1' \longrightarrow {}^2E_2'$ in D_{5h} symmetry.

A significant difference in behaviour between $[NiL^1]^{2+}$ and

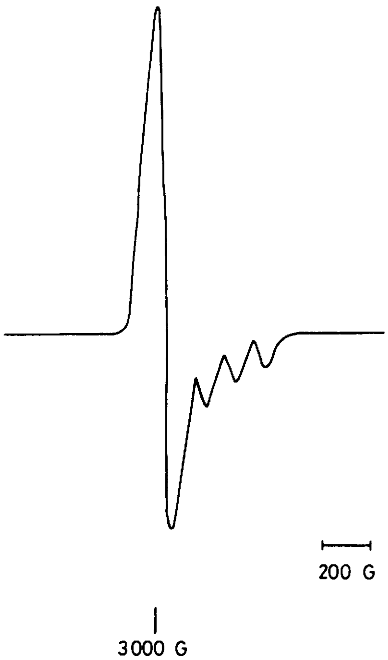

Figure. The powder e.s.r. spectrum of $[CuL^1][BPh_4]_2$

$[NiL^3]^{2+}$ is the stability of the former in solution compared to that of the latter which isomerises to a six-co-ordinate complex of a potentially sexidentate ligand derived from nucleophilic addition of one secondary amine group across an adjacent C=N bond.[5] Such intramolecular ligand rearrangement is, of course, impossible for L^1.

While the incidence of seven-co-ordination[6] in first-row transition-metal chemistry has grown significantly in recent years as a result of the use of specially designed ligands,[4,7-9] seven-co-ordinate compounds are still relatively uncommon. This is particularly true for nickel(II)[4,8,9] and copper(II)[4,8] for which there is a crystal-field stabilisation disadvantage in D_{5h} *vis-à-vis* O_h symmetry.[10] The present results extend the number of examples. They also point the way to the synthesis of pentagonal-bipyramidal complexes of other metal ions by use of a readily prepared septidentate ligand.

Dicopper(II) *Complexes of the Macrocyclic Ligand* L^2.—The single Ba^{2+} ion in $BaL^2(ClO_4)_2·3H_2O$ may be replaced by two copper(II) ions to give $Cu_2L^2(ClO_4)_4·H_2O$. Analytical and i.r. data (Table 1) confirmed that the macrocycle remained intact during the transmetallation. No evidence for magnetic coupling between the copper(II) ions was apparent from measurements of the magnetic moment in the temperature range 90—300 K (Table 1). However, when this complex was treated with imidazole (Him) the new dicopper(II) complex $Cu_2L^2(im)(ClO_4)_3·H_2O$ was obtained. On the evidence of its stoicheiometry, the presence in the i.r. spectrum of a band at 960 cm^{-1}, not present in the spectrum of the tetraperchlorate, said to be characteristic of bridging imidazolate anion,[11] the 3 : 1 electrolyte behaviour in solution, and the magnetic properties, it is concluded that the imidazolate group occurs as an intramolecularly bound bridge between the metal centres. The magnetic moment of 1.85 B.M. at 293 K falls smoothly to 1.66 B.M. at 93 K. While accurate determination of the coupling constant J ($2J$ = singlet–triplet separation) would require measurements to lower temperatures, the available data are sufficient to allow calculation of an approximate value of J of -22 ± 3 cm^{-1} for $g = 2.1$ and $N(\alpha) = 60 \times 10^{-6}$ c.g.s. units. This approximate value of J is, within the limits of error, the same as that found for two previously investigated[12] μ-imidazolato-dicopper(II) complexes of related macrocyclic ligands.

Table 2. Electronic spectral data for the complexes in MeCN solution except where stated otherwise

Complex	Band positions[a]/10^3 cm^{-1}
$[FeL^1][ClO_4]_2$	16.2 (840)
$[CoL^1][ClO_4]_2$	22.3 (149), 15.6 (6), 7.0 (4)
$[NiL^1][ClO_4]_2$	16.5 (16), 7.0 (22)
$[CuL^1][BPh_4]_2$ [b]	11.9, 7.4
$Cu_2L^2(ClO_4)_4·H_2O$	14.3 (210)
$Cu_2L^2(im)(ClO_4)_3·H_2O$	15.0 (220)

[a] ε (dm^3 mol^{-1} cm^{-1}) in parentheses. [b] Nujol mull.

Attempts to prepare dimetallic complexes of other metal ions (Mn^{II}, Fe^{II}, Fe^{III}, Co^{II}, or Ni^{II}) in pure form were unsuccessful.

Experimental

2,6-Diacetylpyridine was used as supplied (Aldrich). 3-Oxapentane-1,5-diamine was prepared as follows. Phosphorus tribromide (0.53 mol) was added dropwise to a cooled stirred solution of diethylene glycol (0.68 mol) and pyridine (0.25 mol). A white precipitate developed and the mixture was stirred overnight at room temperature. The precipitate was filtered off and the pale yellow liquor was distilled under reduced pressure (15 mmHg) yielding 1,5-dibromo-3-oxapentane (140 g, 0.60 mol). The dibromide (0.60 mol), potassium phthalimide (1.35 mol), and diethylamine (3 cm^3) were heated together at 140 °C for 3 h. On cooling, the solid mass was broken up and washed with hot water (3 dm^3), and then recrystallised from glacial acetic acid containing some decolourising charcoal, yielding cream-coloured 3-oxapentane-1,5-diphthalimide (128 g, 0.35 mol). This was suspended in refluxing MeOH (1 dm^3) and hydrazine hydrate (62 cm^3, 99—100%) was slowly added producing a brown solution. A white solid separated and, after reflux for 2 h, 10 mol dm^{-3} HCl (144 cm^3) was added. The MeOH was removed by distillation and the white solid filtered off leaving a brown liquor. To this liquor was added NaOH (200 g). The supernatant brown layer was extracted with diethyl ether (1 dm^3) on a continuous-extraction column for 48 h. The ether was removed to leave an oil which was vacuum distilled (90 °C, 1 mmHg) to give the product as a colourless oil (13 g, 0.16 mol). The product was characterised by mass spectral, i.r., and ^1H n.m.r. analysis.

Preparation of the Complexes.—$ML^1(ClO_4)_2$ (M = Mg, Ca, *or* Ba). These were prepared by adding 3-oxapentane-1,5-diamine (0.01 mol) to a solution of 2,6-diacetylpyridine (0.005 mol) and metal perchlorate (0.005 mol) in dry MeOH (150 cm^3) at room temperature. After *ca.* 1 h the solution was concentrated to *ca.* 50 cm^3 and allowed to stand. White or pale yellow crystals separated in *ca.* 20% (Mg), *ca.* 60% (Ca), or *ca.* 50% (Ba) yield.

$BaL^2(ClO_4)_2·3H_2O$. The complex $BaL^1(ClO_4)_2$ was dissolved in dry MeOH at room temperature and then warmed to *ca.* 60 °C. After 1 h the solution was concentrated to give the product as a finely divided white solid in 35—40% yield. Yields were increased slightly if one equivalent of 2,6-diacetylpyridine was present. The ring closure is suppressed in the presence of added 3-oxapentane-1,5-diamine. This explains why no ring-closed product was obtained in the preparation of $BaL^1(ClO)_4$ (see ref. 1).

$[ML^1][ClO_4]_2$ ($M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}$, *or* Zn^{II}). These complexes were prepared in 70—80% yield by reaction of $CaL^1(ClO_4)_2$ (0.001 mol) with the diperchlorate of the appropriate metal (0.001 mol) in MeOH at *ca.* 30 °C. Tetraphenylborates were obtained by metathesis, using $Na[BPh_4]$, in MeOH—MeCN (60 : 40). For the iron(II) complexes all operations were conducted under nitrogen.

$Cu_2L^2(ClO_4)_4 \cdot H_2O$. To a solution of $BaL^2(ClO_4)_2 \cdot 3H_2O$ (4.38×10^{-4} mol) in refluxing MeOH (150 cm^3) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (1.31×10^{-3} mol). After 30 min the solution was concentrated to give the blue-green product in *ca.* 50% yield.

$Cu_2L^2(im)(ClO_4)_3 \cdot H_2O$. Solid imidazole ($5.96 \times 10^{-4}$ mol) was added to a solution of the above tetraperchlorate (2.98×10^{-4} mol) in refluxing MeOH (150 cm^3). After 30 min the solution was concentrated to give dark blue crystals of the product in *ca.* 80% yield.

Physical Measurements.—Magnetic susceptibilities were measured by the Gouy method between 90 and 300 K. E.s.r. spectra of polycrystalline powders were recorded at room temperature with a Decca Xl spectrometer operated at 9 270 MHz with a magnetic field modulation of 100 kHz.

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