Novel Quinaldic Acids for Selective Chelation of Cadmium(II). X-Ray Crystal Structure of [Cd(C$_{18}$H$_{12}$NO$_4$)$_2$](Me$_2$SO)·2H$_2$O

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Quinaldic acids with a phenacyloxy group in the 8-position of the quinoline nucleus show a high selectivity for chelation of cadmium(II) forming eight-co-ordinate complexes where the carbonyl group takes part in the bonding to the metal ion.

Cadmium is a metal of great environmental concern owing to the high toxicity of all its compounds.[1] To allow the removal of the metal from various sources where it may be harmful, the design of ligands capable of selective complexation is of great interest.[2]†

Quinaldic acids are versatile reagents for the recovery of metal ions, in particular Cu^{2+}. The complexing behaviour is, however, strongly influenced by the nature and the position of the substituents.[3] In the course of our investigations of metal-complexing ligands we have now found that quinaldic acid derivatives with a phenacyloxy group in the 8-position of the quinoline nucleus readily form complexes not only with copper ions but also with cadmium ions in acidic aqueous solution. Thus, a 20 mM chloroform solution of ligand (**1a**), prepared by O-alkylation of 8-hydroxyquinoline-2-carbonitrile with p-(1-dodecyl)phenacyl chloride followed by hydrolysis of the nitrile function, extracts 88 and 69% of Cu^{2+} and Cd^{2+}, respectively, from an equal volume of an aqueous

(1) **a**; R = C$_{12}$H$_{25}$
   b; R = H

(2) **a**; n = 1, X = O
   b; n = 3, X = O
   c; n = 4, X = O
   d; n = 5, X = O
   e; n = 1, X = H,OH
   f; n = 0, X = H$_2$

† Cryptands are known that show a remarkably high selectivity for complexation of Cd^{2+} with respect to Zn^{2+}, Co^{2+}, and Ni^{2+}.[2]
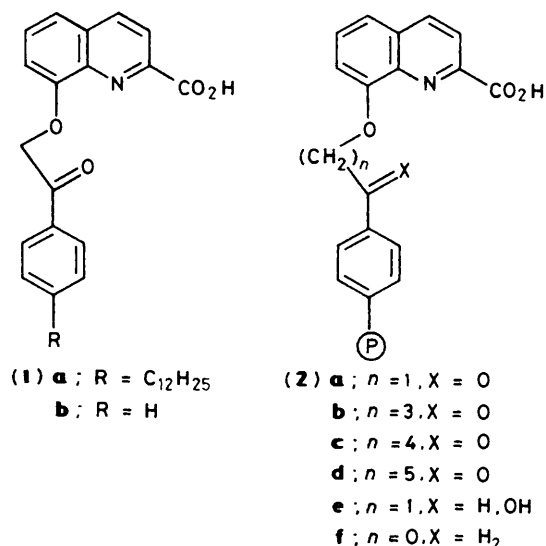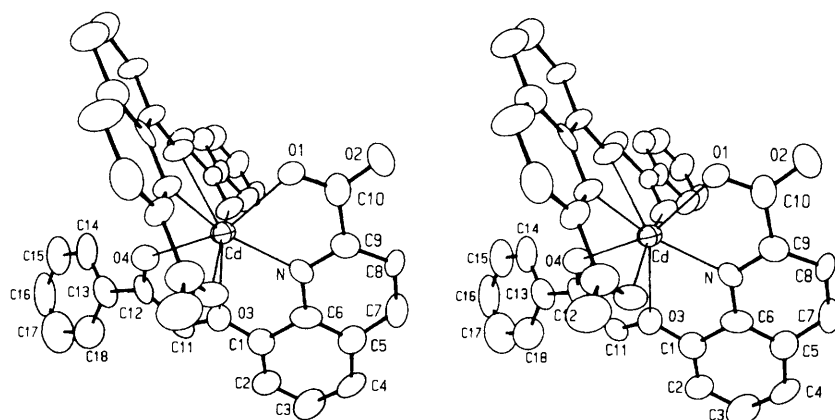
Figure 1. View of the complex showing the atom numbering scheme. (For clarity the numbering scheme for the primed ligand, which is analogous to that for the unprimed ligand, is omitted.) Thermal ellipsoids enclose 50% of probability. Selected bond lengths (Å) and angles (°) [the corresponding values for the primed ligand are given in brackets]: Cd–O(1) 2.32(1) [2.31(1)], Cd–O(3) 2.60(1) [2.58(1)], Cd–O(4) 2.46(1) [2.42(1)], Cd–N 2.34(1) [2.34(1)], N–C(6) 1.38(2) [1.38(2)], N–C(9) 1.34(2) [1.31(2)], C(10)–O(1) 1.23(2) [1.28(2)], C(10)–O(2) 1.27(2) [1.20(2)], C(1)–O(3) 1.35(2) [1.36(2)], C(11)–O(3) 1.40(2) [1.45(2)], C(12)–O(4) 1.20(2) [1.21(1)]; C(6)–N–C(9) 117(1) [119(1)], C(11)–O(3)–C(1) 116(1) [119(1)], O(1)–C(10)–O(2) 123(2) [123(2)].

solution of a mixture of metal sulphates (Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Cd^{2+}, 2 mM in each metal ion), at pH 2. At the same time less than 3% of the other ions is extracted. Replacing Co^{2+} and Ni^{2+} by Fe^{3+} and K^+ results in 65 and 47% extraction of Cu^{2+} and Cd^{2+}, respectively, at pH 1.9, and less than 10% of the other ions. The analogous polymeric reagent (**2a**), prepared *via* grafting of 8-hydroxyquinoline-2-carbonitrile on a chloroacetylated macroporous divinylbenzene polymer, behaves similarly, extracting essentially only Cu^{2+} and Cd^{2+} from the same mixtures of metal sulphates.

The ^{13}C n.m.r. spectrum of a 2 : 1 mixture of compound (**1a**) and $Cd(OAc)_2$ in $CDCl_3$–MeOH (3 : 1) shows shifts of 1.0, 1.9, and 1.7 p.p.m. for the carboxy carbon, the carbonyl carbon, and the CH_2O carbon, respectively, compared to the free ligand. Smaller shifts were observed for protonated aromatic carbons. These observations suggest that the Cd^{2+} ion is co-ordinated to the three different oxygen atoms (carboxy, carbonyl, and ether) and the assumption was verified by an X-ray analysis of the Cd complex with ligand (**1b**), crystallized from dimethyl sulphoxide.‡
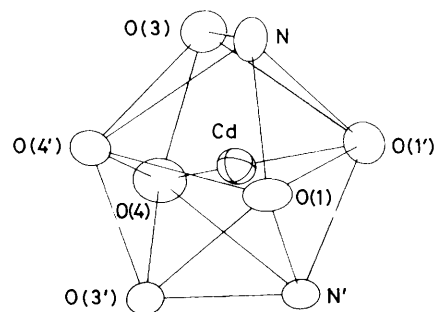
Figure 2. The co-ordination polyhedron at Cd.

A stereoview of the complex is shown in Figure 1. The cadmium atom is eight-co-ordinated by two tetradentate ligands. This rather unusual co-ordination results from the rigid structure of the ligand. The co-ordination polyhedron can be described as a distorted dodecahedron (Figure 2). Within the limits of error the two ligands co-ordinate to Cd^{II} in an identical manner, with a dihedral angle of 90(2)° between the least-squares planes N, O(1), O(3), O(4) and N', O(1'), O(3'), O(4') and a maximum displacement of ±0.09 and ±0.06 Å from the best planes, respectively (Figure 2). The ligands have three different types of oxygen involved in the bonding to Cd^{II}, at the average distances Cd–O(1) (carboxylate) 2.32(1), Cd–O(3) (ether) 2.44(1), and Cd–O(4) (carbonyl) 2.59(1) Å. The average Cd–N distance is 2.34(1) Å. The Cd–O (carboxylate, ether) and Cd–N distances are comparable to distances found in other eight-co-ordinated Cd^{II} complexes.[4—6] The Cd–O(4) (carbonyl) distance is 0.2 Å longer than the distance found in a six-co-ordinated Cd^{II} complex,[7] which is reasonable because of the difference in co-ordination number. Although the two ligands co-ordinate to Cd^{II} in the same way, the conformations of the individual ligands are not identical. The most significant differences are: (i) the ligands are non-planar with a dihedral angle of 12.0(2)° for the primed, and 38.8(7)° for the unprimed ligand, between the quinoline and phenyl groups; (ii) the torsion angles C(2)–C(1)–O(3)–C(11) and C(11)–C(12)–C(13)–C(14) are $-9(2)$ and 179(1)° for the primed and $-25(2)$ and 145(2)° for the unprimed ligand. The quinoline and phenyl groups are planar within 0.04(2) Å. Bond distances and angles in the ligands are as expected.

The crystal is built up from discrete Cd^{II} complexes, water, and Me$_2$SO (solvent) molecules. It is stabilized by van der Waals' interactions and hydrogen bonds involving water, the carboxylate oxygen atoms O(2) and O(2'), and Me$_2$SO.

To study further the influence of the carbonyl group on the cadmium selectivity, the polymer-supported reagents (2b—f) were prepared and tested for their ability to extract metal ions. Polymers (2b—d) were prepared analogously to reagent (2a), by reaction of 8-hydroxyquinoline-2-carbonitrile with poly-divinylbenzene that had been acetylated with the appropriate ω-bromoalkanoyl chloride, followed by hydrolysis, while (2e) was prepared by sodium borohydride reduction of (2a). Polymer (2f), finally, was obtained by reaction of chloro-methylated polydivinylbenzene with 8-hydroxyquinoline-2-carbonitrile, followed by hydrolysis.

All the chelating ion exchange resins (2b—f) showed a dramatic decrease of the adsorption of cadmium compared to (2a). These reagents adsorbed only Cu^{2+} to a large extent at pH 2, except for (2e), which retained some ability to extract Cd^{2+} (36% at pH 2) and (2c), which in addition to Cu^{2+} also adsorbed Zn^{2+} (34% at pH 2). The latter observation is in accord with our previous findings that certain 8-alkoxyquinal-dic acids show a high selectivity for Zn^{2+}.[3] The high tendency of (1a) and (1b) to complex Cd^{2+} is therefore believed to be due to the ability of these ligands to form eight-co-ordinate complexes.

Further details about the properties and applications of these new reagents, e.g. for removal of Cd^{2+} from phosphoric acid containing a 25-fold excess of Ca^{2+}, will be reported in a full account.

References

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