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Metal–Phenoxyalkanoic Acid Interactions.
Part 19*. The Divalent Metal Complexes of 2-Carboxyphenoxyacetic Acid and the Crystal Structures of *catena-μ-*[(2-carboxylato-O)phenoxyacetatoaquacopper(II)] and Diaquabis(2-carboxyphenoxyacetato)copper(II)

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Abstract

The crystal structures of two chemical polymorphs of copper(II) 2-carboxyphenoxyacetate ($OCPAH_2$) have been determined by X-ray diffraction. The first complex with formula $[Cu(OCPA)(H_2O)]_n$ (1) is a step polymer with inversion related square pyramidal copper centres comprising an axial water molecule [Cu–Ow, 2.192(8) Å], two oxygens from a bidentate chelate phenoxy group [Cu–O(carboxyl), 1.921(9) Å; Cu–O(ether), 2.050(7) Å], an oxygen from the 2-carboxyl group [Cu–O, 1.906(8) Å] and one from a bridging carboxylate group [Cu–O, 1.941(8) Å]. Polymorph (2) $[Cu(OCPAH)_2(H_2O)_2]$, is square planar with two waters [Cu–Ow, 1.912(10) Å], and *trans*-related phenoxy ligands [Cu–O, 1.912(10) Å] bonded to the metal through the phenoxy carboxyl group. The 2-carboxyl group is protonated and forms cyclic hydrogen bonds with adjacent complex units [O–O, 2.92 Å] to give a stable polymer network. Data also confirms isomorphism in the divalent OCPA complexes of Co, Ni and Mg, having the formula $[M(OCPA)(H_2O)_3]$.

Introduction

In a continuing study of the divalent metal complexes of the phenoxyalkanoic acids, the presence of an *ortho* substituent on the phenoxy ring has been of particular interest. Although a chloro group appears to influence the formation of unusual complexes [2, 3], other groups such as nitro[4], carbamoyl [5] or formyl [1] are relatively stereotypical, none appearing to involve the second functional group in coordination. However, when the second group is a carboxyl group, a potentially three donor chelate system is available for metal coordination. This article reports the crystal structures for two chemical polymorphs of Cu^{II} and 2-carboxyphenoxyacetic acid ($OCPAH_2$), $[Cu(OCPA)(H_2O)]_n$ (1) and $[Cu(OCPAH)_2(H_2O)_2]$ (2), together with data for the divalent Co, Ni and Mg complexes $[Co(OCPA)(H_2O)_3]$ (3), $[Ni(OCPA)(H_2O)_3]$ (4) and $[Mg(OCPA)(H_2O)_3]$ (5).

Experimental

Preparation of Complexes

Complexes were all prepared by reacting a hot aqueous solution of a neutral salt of 2-carboxyphenoxyacetic acid with an aqueous solution of the appropriate metal(II) acetate in 1:1 molar ratio, using the recognised procedure [6]. Room temperature evaporation of the solution formed with the copper(II) salt gave initially small blocky pale blue/green crystals of polymorph (1) which were removed by filtration. Further crystallization from a more concentrated solution yielded dark blue needles of polymorph (2). With complexes (3)–(5), precipitation of well-formed crystals occurred on cooling the solutions. Twinning is a common feature with all compounds but was overcome to a large extent in (1) and (2) allowing collection of X-ray intensity data. However the problem was not resolved in complexes (3)–(5) but elemental analysis, infrared spectroscopy and single crystal X-ray diffraction have confirmed an isomorphous series with formula $[M(OCPA)(H_2O)_3]$. *Anal.* $[Cu(OCPA)(H_2O)]_n$ (1). Found: C, 39.1; H, 2.97%. Calc. for $C_9H_8CuO_6$: C, 39.2; H, 2.92%. $[Cu(OCPAH)_2(H_2O)_2]$ (2). Found: C, 44.3; H, 4.22%. Calc. for $C_{18}H_{18}CuO_{12}$: C, 44.1; H, 3.68%. $[Co(OCPA)(H_2O)_3]$ (3). Found: C, 35.3; H, 4.00%. Calc. for $C_9H_{12}CoO_8$: C, 35.2; H, 3.94%. $[Ni(OCPA)(H_2O)_3]$ (4). Found: C, 35.4; H, 4.02%. Calc. for $C_9H_{12}NiO_8$: C, 35.2; H, 3.94%. $[Mg(OCPA)(H_2O)_3]$ (5). Found: C, 39.7; H, 4.50%. Calc. for $C_9H_{12}MgO_8$: C, 39.8; H, 4.45%.

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*Part 18 is ref. 1.

TABLE I. Cell Data for $[Cu(OCPA)(H_2O)]_n$ (1) and $[Cu(OCPAH)_2(H_2O)_2]$ (2)

	(1)	(2)
Formula	$C_9H_8CuO_6$	$C_{18}H_{18}CuO_{12}$
M_r	275.7	489.5
a (Å)	8.415(2)	4.086(5)
b (Å)	6.822(1)	9.954(12)
c (Å)	17.039(3)	12.469(12)
α (°)		72.87(9)
β (°)	103.65(2)	88.63(9)
γ (°)		82.74(10)
V (Å^3)	950.8	480.7
Z	4	1
D_c	1.924	1.691
D_m (g cm^{-3})	1.92	1.69
F(000)	556	251
μ (cm^{-1})	24.0	12.5
Space group	$P2_1/n$	$P\bar{1}$
Data collection		
Diffractometer	Nicolet R3m	Nicolet R3m
Radiation	Mo Kα	Mo Kα
Wavelength (Å)	0.71069	0.71069
$2\theta_{max}$ (°)	50	50
Crystal dimensions (mm)	0.20 × 0.12 × 0.12	0.25 × 0.18 × 0.12
Structure solution refinement		
Method used	Patterson	Heavy atom/Fourier
R	0.057	0.100
R_w	0.057	unit weights
w^a A	1.14×10^{-3}	–
Data used	794	517
Discrimination	$I > 2.5\sigma(I)$	$I > 1.0\sigma(I)$

$^a w = [\sigma^2 Fo + A(Fo)^2]^{-1}$.

Crystallography

Crystal data and details of structure solution and refinement for **(1)** and **(2)** are given in Table I. Data were collected on a Nicolet R3m four-circle diffractometer and the structures were solved by heavy atom and Fourier methods using the SHELXTL [7] structure solution package on the Nicolet. For **(1)**, anisotropic thermal parameters were used for all heavy atoms while for **(2)**, because of the poor quality of the data, atoms were treated isotropically. Hydrogen atoms were located from difference-Fourier syntheses and included in the refinements at fixed positions with their isotropic U values set invariant at 0.05 Å^2. Neutral atom scattering factors were used [8] while heavy atoms were corrected for the effects of anomalous dispersion [8]. Final residuals R and R_w are defined as follows:

$$R = [\Sigma|F_o - F_c|/|F_o|]$$

$$R_w = [(\Sigma w|F_o - F_c|^2/\Sigma w|F_o|^2)^{1/2}]$$

Atomic coordinates, and bond distances and angles are given in Tables II and III, respectively, while observed and calculated structure factors and anisotropic thermal parameters are available from the authors.

Discussion

$[Cu(OCPA)(H_2O)]_n$ (1)

The structure of polymorph **(1)** involves copper(II) in square pyramidal five-coordination (Fig. 1). The distorted square plane consists of two oxygens of the oxoacetic acid residue of the ligand in a bidentate chelate mode [Cu–O(ether, 2.050(7) Å; Cu–O(carboxyl), 1.921(9) Å] and an oxygen from the 2-carboxylate group [Cu–O, 1.906(8) Å]. The second carboxylato oxygen of this group at (½ – x, ½ + y, ½ – z) links adjacent complex units through the fourth coordination position [Cu–O, 1.941(8) Å] to form a step polymer (Fig. 2). The single water in the complex occupies the axial position of the square pyramid [Cu–Ow, 2.192(8) Å]. The shortness of the Cu–O(ether) bond represents substantial

TABLE II. Atomic Coordinates (× 10^4) and Isotropic/Equivalent Isotropic Thermal Parameters (Å^2 × 10^3)

	(1) $[Cu(OCPA)(H_2O)]_n$				(2) $[Cu(OCPAH)_2(H_2O)_2]$			
	x/a	y/b	z/c	U_{eq}^*/iso^a	x/a	y/b	z/c	U_{eq}^*/iso^a
Cu	4146(2)	6318(2)	7210(1)	31.8(5)*	0	10000	0	38(5)
Ow	6138(9)	4198(11)	7300(5)	42(3)*	3567(12)	9204(12)	–737(6)	49(3)
C(1)	2658(13)	5159(17)	5424(7)	25(4)*	759(15)	4390(20)	3186(8)	23(5)
C(2)	1873(13)	3620(16)	5705(6)	27(4)*	15(15)	3551(20)	2531(8)	26(5)
C(3)	1009(14)	2290(19)	5121(6)	41(5)*	588(16)	2119(19)	2942(8)	30(5)
C(4)	980(15)	2489(19)	4316(7)	42(5)*	2206(16)	1496(18)	3968(8)	46(5)
C(5)	1785(14)	3991(17)	4064(7)	38(4)*	3201(16)	2311(19)	4612(8)	36(5)
C(6)	2623(14)	5341(20)	4604(7)	35(4)*	2444(16)	3809(20)	4218(8)	26(5)
O(7)	3525(10)	6493(12)	5973(4)	38(3)*	17(15)	5859(15)	2773(7)	34(4)
C(8)	5858(16)	1748(15)	4321(6)	37(4)*	2017(16)	6759(20)	3097(9)	34(5)
C(9)	4886(15)	579(20)	3601(7)	38(5)*	2248(16)	8173(19)	2134(8)	46(5)
O(10)	4601(10)	1391(12)	2907(5)	38(3)*	517(14)	8268(15)	1204(6)	42(5)
O(11)	5595(12)	1054(14)	6248(5)	56(4)*	3201(14)	9121(15)	2367(6)	47(5)
C(21)	1801(15)	3277(17)	6555(7)	25(4)*	–2156(16)	4153(18)	1458(8)	25(5)
O(111)	2614(10)	4233(11)	7145(4)	38(3)*	–2560(14)	5577(14)	955(5)	37(5)
O(112)	894(10)	1859(12)	6676(5)	35(3)*	–3086(14)	3331(14)	1019(6)	47(5)

$^a U_{eq}^* = (U_{11} \times U_{22} \times U_{33})^{1/3}$.

TABLE III. Bond Distances (Å) and Angles (°) for (1) and (2)

Coordination sphere	
(a) Distances	
(1)	
Cu–Ow	2.192(8)
Cu–O(7)	2.050(7)
Cu–O(10)	1.921(9)
Cu–O(112)′	1.941(8)
Cu–O(111)	1.906(8)
(2)	
Cu–Ow	1.912(10)
Cu–O(10)	1.912(10)
(b) Angles	
(1)	
Ow–Cu–O(7)	96.7(3)
Ow–Cu–O(10)	96.6(3)
Ow–Cu–O(112)′	104.2(3)
Ow–Cu–O(102)	90.4(3)
O(7)–Cu–O(10)	82.0(3)
O(7)–Cu–O(112)′	159.1(4)
O(7)–Cu–O(111)	88.8(3)
O(10)–Cu–O(112)′	94.8(4)
O(10)–Cu–O(111)	168.9(3)
O(11)–Cu–O(111)	91.7(3)
Cu–O(10)–C(9)	117.4(7)
Cu–O(111)–C(21)	131.9(8)
Cu–O(111)′–C(21)′	116.8(7)
Cu–O(7)–C(1)	128.5(7)
Cu–O(7)–C(8)	112.3(6)
(2)	
Ow–Cu–O(10)	88.1(6)
Cu–O(10)–C(9)	120.2(9)

Intraligand		
(a) Distances	(1)	(2)
C(1)–C(2)	1.38(2)	1.39(2)
C(1)–C(6)	1.40(2)	1.40(2)
C(1)–O(7)	1.38(1)	1.39(2)
C(2)–C(3)	1.41(1)	1.35(2)
C(2)–C(21)	1.48(2)	1.54(2)
C(3)–C(4)	1.37(2)	1.38(2)
C(4)–C(5)	1.35(2)	1.39(2)
C(5)–C(6)	1.37(2)	1.42(2)
O(7)–C(8)	1.44(1)	1.43(2)
C(8)–C(9)	1.52(2)	1.57(2)
C(9)–O(10)	1.21(1)	1.34(2)
C(9)–O(11)	1.23(2)	1.17(2)
C(21)–O(111)	1.26(1)	1.21(2)
C(21)–O(112)	1.28(1)	1.36(2)
(b) Angles	(1)	(2)
C(2)–C(1)–C(6)	121(1)	122(1)
C(2)–C(1)–O(7)	119(1)	119(1)
C(6)–C(1)–O(7)	120(1)	119(1)
C(1)–C(2)–C(3)	117(1)	120(1)
C(1)–C(2)–C(21)	126(1)	122(1)
C(3)–C(2)–C(21)	117(2)	117(1)
C(2)–C(3)–C(4)	118(1)	120(1)
C(3)–C(4)–C(5)	120(1)	121(1)
C(4)–C(5)–C(6)	121(1)	119(1)
C(5)–C(6)–C(1)	120(1)	118(1)
C(1)–O(7)–C(8)	119(1)	120(1)
O(7)–C(8)–C(9)	109(1)	112(1)
C(8)–C(9)–O(10)	118(1)	113(1)
C(8)–C(9)–O(11)	116(1)	118(1)
O(10)–C(9)–O(11)	126(1)	126(1)
C(2)–C(21)–O(111)	124(1)	118(1)
C(2)–C(21)–O(112)	116(1)	119(1)
C(111)–C(21)–O(112)	120(1)	122(1)

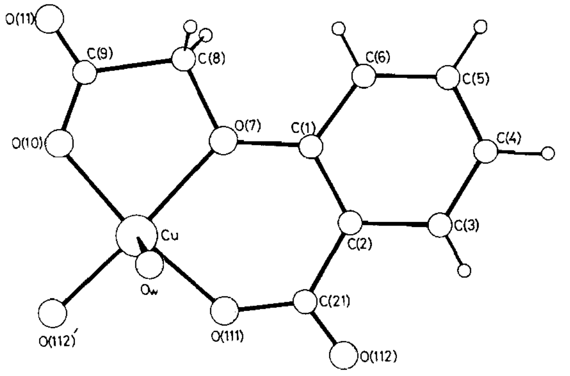

Fig. 1. Molecular configuration for the repeating monomer unit in $[Cu(OCPA)(H_2O)]_n$ (1).

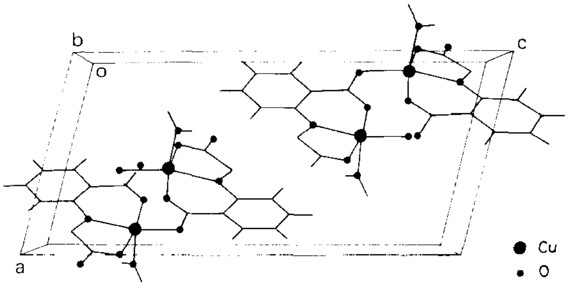

Fig. 2. Packing of (1) in the unit cell.

strengthening of this bond compared to other examples among the metal phenoxyalkanoates. With the tetragonally distorted copper(II) complexes of the type $[Cu(4\text{-}X\text{-}C_6H_4OCH_2COO)_2(H_2O)_n]_m$, the elongated axial positions of the coordination sphere are invariably occupied by the ether oxygens of the two phenoxy ligands [(Cu–O(ether) distances for: X = H, 2.48 Å [9]; 2.47 Å [10]; X = F, 2.47 Å [11]; X = Cl, 2.41 Å [12]; X = OMe, 2.43 Å [13]]. Similarly, in the polymeric zinc phenoxyisobutyrate complex $[Zn_5(PIBA)_{10}(H_2O)_2]_n$, which has three independent coordination sites, (two octahedral and one trigonal bipyramidal), two of the bidentate chelate ligands are associated with one distorted octahedral centre [Zn–O(ether), 2.20, 2.30 Å] while the third five-coordinate centre has the ether oxygen occupying the axial position [Zn–O, 2.38 Å] [14].

With the more closely related complexes of benzene-1,2-dioxydiacetic acid ($BDDAH_2$), $Na[La(BDDA)_2(H_2O)_2]$ [15], $[K(BDDAH)(BDDAH_2)]$, [16], $[Zn(BDDA)(H_2O)_3]\cdot 3.5H_2O$ [17] and the isomorphous $[Ca(BDDA)(H_2O)_2]_n\cdot nH_2O$ and $[Mn(BDDA)(H_2O)_2]_n\cdot nH_2O$ [17], coordination about a pentagonal plane involves two long metal–O(ether) links.

The phenyl ring of the OCPA ligand is almost coplanar with the square plane of the metal complex while the 2-carboxyl group is similarly close to coplanar [torsion angle C(1)–C(2)–C(21)–O(111), −8.7°]. This is also consistent with the tendency for the BDDA ligand to remain essentially planar in the complexed state [15, 16, 17]. The *exo* ring angles at C(1) are unchanged compared with the values for the 'free' acids and complexes including (2) in which the ligand is unconstrained [12]. In these, the C(6)–C(1)–O(7) angle is invariably enlarged. It would appear that the distortion is transferred to the 2-carboxy group where the angles are 126, 117(2)°, compared with those for (2) (unidentate) [122, 117(1)°]. The structure of (1) is stabilized by a single hydrogen bonding contact between the coordinated water and the uncoordinated phenoxy oxygen [O(11)] of an adjacent complex centre [O···O, 2.76 Å] while other short intermolecular O···O contacts involving O(112) exist [O(102), 2.76 Å; O(10), 2.84 Å]. A relatively long contact between copper and a carboxylate oxygen [O(102)] is also found (2.85 Å).

[Cu(OCPAH)$_2$(H$_2$O)$_2$] (2)

Complex (2) is square planar and centrosymmetric with both Cu–O distances equal [1.912(10) Å]. The coordination involves two waters and two unidentate carboxylate oxygens from the oxoacetate residues of the ligands (Fig. 3). The 2-carboxy groups of each ligand are not involved in coordination but form relatively long (2.92 Å) cyclic hydrogen bonded contacts (as found in most carboxylic acids) with the equivalent group of an adjacent complex unit ($1 - x$, $1 + y$, z). This results in an extended zig-zag chain of complexes along the *b* direction in the unit cell (Fig. 4).

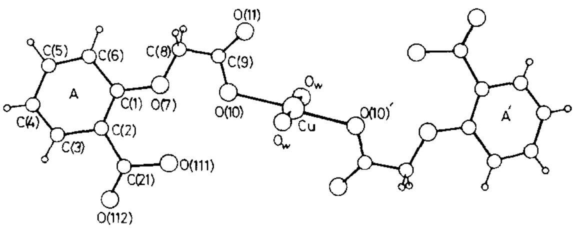

Fig. 3. Molecular configuration for $[Cu(OCPAH)_2(H_2O)_2]$. Primed atoms are generated by an inversion operation.

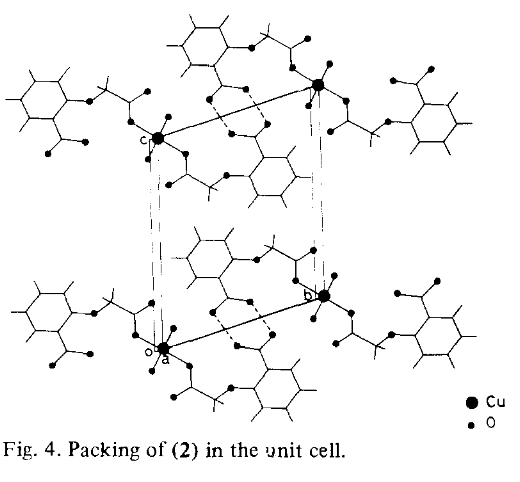

Fig. 4. Packing of (2) in the unit cell.

As in (**1**), the oxoacetate side-chain is approximately planar [torsion angles C(2)–C(1)–O(7)–C(8), –149°; C(1)–O(7)–C(8)–C(9), +147.2°; O(7)–C(8)–C(9)–O(11), +163.9°] while the 2-carboxy group is also essentially coplanar [torsion angle C(1)–C(2)–C(21)–O(111), +19.5°]. The plane of the ligand is in turn approximately perpendicular to the complex square plane. Internal hydrogen bonding interactions involving the waters further stabilizes the packing in the unit cell: Ow(1)····O(11), 2.66 Å; ····O(101), 2.67 Å; ····O(10), 2.75 Å.

This mode of complexation is also found for diaquabis(4-methoxyphenoxyacetato)copper(II) dihydrate [13] and diaquabis(2-carbamoylphenoxyacetato)copper(II) [5], while it is likely that diaquabis(2-formylphenoxyacetato)copper(II) [1] is also square planar. In the case of polymorph (**2**), the 2-carboxy group has a greater tendency to coordinate than the carbamoyl or formyl groups so that the reason for its non-involvement in coordination could be interpreted as a pH effect since the method of preparation invariably results in unreacted acid in the crystallizing solution. This has resulted in some instances in the formation of complex adducts having uncomplexed acid molecules [11, 18].

The mode of complexation resulting in square pyramidal coordination (polymorph **1**) appears to be preferred in the case of copper(II) which is less inclined to assume the pentagonal planar systems found in the La, Ca, Mn or Zn complexes of $BDDAH_2$. In these, the duplication of the oxoacetic acid residue at the 2-position compared to the carboxylate group of $OCPAH_2$ results in a relatively rigid four-donor chelate system. The constraints of this system favour the more open positions of the regular pentagon with the remaining site being occupied by water or a bridging acetate group. With the copper(II) complex of $BDDAH_2$ [17] [formula $[Cu(BDDA)(H_2O)_4]$], it is likely that it too is similar to complex (**1**), despite the exclusive formation with $BDDAH_2$ of pentagonal bipyramidal [1:1] complexes of metal(II) ions. The 1:2 complex of nickel(II), $[Ni(BDDAH)_2(H_2O)_4]$ [17] is a conventional octahedral species.

Elemental analysis, infrared spectroscopy together with preliminary X-ray diffraction data indicate that the series $[M(OCPA)(H_2O)_3]$ M = Co (**3**); Ni (**4**); Mg (**5**)] is isomorphous but different from (**1**) or (**2**). It is likely that this series is based upon an octahedral stereochemistry for the metal with the OCPA ligand occupying three coordination positions about the square plane and the three meridional waters completing the six-coordination.

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References

1 C. H. L. Kennard, E. J. O'Reilly, G. Smith and T. C. W. Mak, *Aust. J. Chem., 38,* 138 (1985).
2 C. H. L. Kennard, E. J. O'Reilly and G. Smith, *Polyhedron, 3,* 689 (1984).
3 G. Smith, E. J. O'Reilly, C. H. L. Kennard and A. H. White, *J. Chem. Soc., Dalton Trans.,* 243 (1985).
4 C. H. L. Kennard, S. W. Stewart, E. J. O'Reilly, G. Smith and A. H. White, *Polyhedron, 4,* 697 (1985).
5 T. C. W. Mak, W.-H. Yip, G. Smith, E. J. O'Reilly and C. H. L. Kennard, *Inorg. Chim. Acta, 112,* 53 (1986).
6 C. H. L. Kennard, G. Smith, E. J. O'Reilly and P. T. Manoharan, *Inorg. Chim. Acta, 82,* 35 (1984).
7 G. M. Sheldrick, 'SHELXTL User Manual, Revision 3', Nicolet XRD Corporation, Cupertino, Calif., 1981.
8 J. A. Ibers and W. C. Hamilton (eds.), 'International Tables for X-ray Crystallography, Vol. 4', Kynoch Press, Birmingham, 1974.
9 C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust and F. J. C. Rossotti, *J. Chem. Soc., A:,* 2791 (1968).
10 J. R. Carruthers, K. Prout and F. J. C. Rossotti, *Acta Crystallogr., Sect. B:, 31,* 2044 (1975).
11 E. J. O'Reilly, G. Smith and C. H. L. Kennard, *Inorg. Chim. Acta, 90,* 63 (1984).
12 G. Smith, E. J. O'Reilly, C. H. L. Kennard, K. Stadnicka and B. Oleksyn, *Inorg. Chim. Acta, 47,* 111 (1981).
13 C. K. Prout, P. J. Grove, B. D. Harridine and F. J. C. Rossotti, *Acta Crystallogr., Sect. B:, 31,* 2047 (1975).
14 G. Smith, E. J. O'Reilly, C. H. L. Kennard and T. C. W. Mak, *Inorg. Chem., 24,* 2321 (1985).
15 H. B. Kerfoot, G. R. Choppin and T. J. Kistenmacher, *Inorg. Chem., 18,* 787 (1979).
16 E. A. Green, W. L. Duax, G. M. Smith and F. Wudl, *J. Am. Chem. Soc., 97,* 6689 (1975).
17 G. Smith, E. J. O'Reilly and C. H. L. Kennard, unpublished results.
18 C. H. L. Kennard, G. Smith, E. J. O'Reilly and K. E. Brown, *Inorg. Chim. Acta, 52,* 55 (1981).